FAMOUS CHEMISTS

E. ROBERTS, B. Sc.

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BY

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PREFACE

The object of this little book is to give an account of the chief work of the most famous chemists, and to indicate briefly the part played by each in the development of the Science.

The following books have been frequently consulted :—

History of Chemistry	Ladenburg.
Heroes of Science	Pattison Muir.
Liebig	Shenstone.
Essays in Historical Chemistry	T. E. Thorpe.
Treatise on Chemistry, vol. 1 and 2	Roscoe & Schorlemmer.
Progress of Chemical Philosophy	Brande.
Rise and Development of Organic Chemistry	Schorlemmer.
Memorial Lectures delivered before the Chemical Society.	

E. ROBERTS.

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Famous Chemists

GEORGE ERNEST STAHL

1660-1734

George Ernest Stahl was born at Anspach, 21st October, 1660. He studied for his degree of Doctor of Medicine at Jena, and graduated there in 1683. In 1687 he became physician to the Duke of Weimar, and in 1694 was made Professor of Anatomy, Medicine and Chemistry at the University of Halle. Stahl was one of the most eminent physicians of his day, and in 1716 was appointed physician in ordinary to the King of Prussia. He died at Berlin, May 4th, 1734.

Becher (1635-1682) was the first to suggest that combustible bodies are compounds, and to attribute the phenomena of heat and light to the escape of the combustible constituent. Stahl was a pupil, and afterwards a friend of Becher, and developed the views of his teacher into a complete theory of combustion—the Phlogiston Theory—which dominated the chemical world for nearly a century.

According to Stahl every substance consists of phlogiston and something else, and when the substance burns the phlogiston is thrown into violent motion and escapes in the form of flame, the other constituent of the body remaining behind.

Sulphur consists of Sulphuric acid and phlogiston.

A metal consists of its calx (oxide) and phlogiston.

Soot is nearly pure phlogiston, that is why when it is heated with a metallic calx the metal is regenerated.

Stahl tried to prove that the phlogiston of soot and sulphur are identical. He argued in this way: Sulphur consists of sulphuric acid + phlogiston, hence if phlogiston can be added to sulphuric acid sulphur will result. To test his theory he rendered sulphuric acid non-volatile (fixed) by combining it with potash, and heated the solid substance thus formed (potassium sulphate) with charcoal, and obtained "liver of sulphur;" he dissolved this in water and treated with acids and obtained sulphur according to his expectations, and therefore concluded that the phlogiston in sulphur is identical with that in soot. Further, since metals are regenerated by heating their calxes with soot, he assumed that the phlogiston in metals, sulphur, and soot is the same.

Even as early as the eighth century Geber had noticed that lead and tin increase in weight on combustion, and that the calxes of lead and tin weigh more than the respective metals. Stahl was aware of this, but regarded the increase of weight as unimportant.

Although the Phlogiston Theory was erroneous, it served a useful purpose by grouping together similar phenomena, and it certainly contributed towards the advancement of knowledge ; indeed, according to Roscoe and Schorlemmer, " It is only after Stahl's labours that a scientific chemistry becomes, for the first time, possible."

ROBERT BOYLE

1627-1691

ROBERT BOYLE was the seventh son of the Earl of Cork, and was born at Lismore, in the county of Waterford, 1627.

When he was eight years old he was sent to Eton, but left at the age of twelve to travel on the Continent with an elder brother, and remained there until his father's death six years later. For some time after this event Boyle lived quietly at his manor of Stalbridge, Dorsetshire, engrossed in his books and laboratory. He moved to Oxford in 1654 and died 1691.

Robert Boyle may be called the first truly scientific chemist, since he was the first to teach that chemistry ought to be studied for the love of knowledge for its own sake, and that this science should not be regarded merely as a means of discovering substances to use as medicines, or for industrial purposes.

By his great book, "The Sceptical Chymist," he overthrew the Paracelsian doctrine of the "tria prima," mercury, sulphur, and salt. He was the first to grasp the distinction between elements and compounds, and to use these terms in their modern sense. He overthrew the theory that dry distillation resolves a substance into its elements, by distilling wood and obtaining two substances, methyl alcohol and pyroligneous acid, from the liquid distillate. He was the first to prepare acetone by heating the acetates of lead and lime.

He showed that calxes of the metals are heavier than the metals themselves by heating tin and lead in sealed vessels containing air, and performed many experiments for "the arresting and weighing of igneous corpuscles," but owing to his belief in the material nature of flame and fire, he did not grasp the true reason for the observed increase in weight. He discovered Boyle's law—"The volume of a given mass of gas varies inversely as the pressure, the temperature remaining constant." He proved that the rise and fall of the mercury column in a barometer is due to variation of atmospheric pressure, and showed that the boiling point of a liquid depends upon the pressure to which it is subjected.

JOSEPH BLACK

1728-1799

Joseph Black was born near Bordeaux, 1728, but his parents were Scotch. At the age of twelve he went to school at Belfast, and six years afterwards to Glasgow, where he studied medicine. About 1750 he went to Edinburgh University to finish his medical training, and graduated as M.D. in 1755. Shortly afterwards he was appointed Professor of Anatomy and Lecturer on Chemistry in Glasgow University. In 1766 he obtained the post of Professor of Chemistry in the University of Edinburgh, which he retained until his death in 1799.

At the beginning of the eighteenth century, the mild or fixed alkalis (carbonates) were supposed to be simpler substances than the caustic alkalis. It was also known that when quicklime was heated with fixed alkalis (potassium or sodium carbonate) these were transformed into caustic alkalis, and it was supposed that quicklime (prepared by strongly heating limestone) acquired this property (viz: of converting mild into caustic alkalis) during its formation from limestone, and that it was due to a "power" or "igneous matter" derived from the fire.

Black attempted to discover the nature of this "igneous matter," and found that when a weighed quantity of limestone was heated, the quicklime derived from it weighed *less* than the limestone from which it was derived. He then experimented with mild magnesia (magnesium carbonate.) He strongly heated a weighed quantity in a retort connected with a receiver, and noticed that nothing visible collected in the receiver except a few drops of water, weighing much less than the difference between the weights of the residue in the retort and the weight of carbonate originally taken. He concluded that the discrepancy was due to some gas that had been given off by the magnesium carbonate.

He next dissolved some mild magnesia in acids, and noticed that effervescence occurred, which he thought was probably due to the same kind of "air," or gas, that was given off by heat. He proceeded to prove this.

He calcined a weighed quantity of magnesium carbonate, dissolved the residue in dilute sulphuric acid, then mixed with fixed alkali (potassium carbonate) collected the precipitated solid, washed and weighed it; the weight was practically the same as that of the magnesium carbonate originally taken; the substance also possessed the same properties.

He collected the air (which he called "fixed air,") evolved during the calcination of the magnesium carbonate, and showed that the same air is expired by animals, and given off during vinous fermentation; it cannot support life. He obtained a similar "air" by calcining chalk, and believed that chalk and magnesia had similar properties.

He showed that quicklime is entirely soluble in water, and that it is a definite substance which can combine with "fixed air," when it becomes another definite substance—chalk. Black also examined the phenomena of heat and cold, and discovered "latent heat."

Black was a careful worker, persevering and thorough, and was the first to establish chemical results by means of the balance. He was an excellent teacher, materially advanced the science of chemistry by his able lectures, and was one of the first to accept and teach Lavoisier's theory of combustion. By his rediscovery of carbonic acid gas he aroused interest in this branch of chemistry.

HENRY CAVENDISH

1731-1810

HENRY CAVENDISH, the son of Lord Charles Cavendish, was born at Nice in 1731 and died in London, 1810. He had wealth and leisure, and devoted his life to scientific investigations. He had great natural ability, in fact he was one of the cleverest men of his age, but he was painfully shy and hated publicity, and on this account suppressed many of his discoveries, even after he had prepared memoirs for publication.

His first investigations were in connection with heat. He mixed weighed quantities of water at different temperatures, and took the temperature of the resulting mixture. Then he tried the effect of mixing quicksilver and water at different temperatures, and found that it required a greater weight of quicksilver than water, at the same temperature, to cool a given weight of hot water to a given temperature. He also made similar experiments with metals, sulphur, glass and other substances, and concluded "that the true explanation of these phenomena seems to be that it requires a greater quantity of heat to raise the heat of some bodies a given number of degrees by the thermometer than it does to raise other bodies the same number of degrees." Cavendish made this discovery in 1764, but did not make it public then, and so others, though later in the field, are usually regarded as the discoverers of specific heat.

Cavendish greatly improved the thermometer, and showed that a correction must be applied when the whole column of mercury is not immersed in the liquid, gas, etc., of which it is desired to ascertain the temperature. He devoted a great deal of time and care to phenomena connected with heat, and determined the freezing point of quicksilver.

Up to the middle of the 18th century chemists thought that all gases were modifications of common air; then Black showed that "fixed air," or carbon-dioxide as we now call it, is quite different to the air we breathe. Cavendish also investigated this gas and published an account of its properties in 1766. He showed that though cold water readily absorbs the gas, it is expelled by boiling, and he applied this fact to explain the formation of "fur" in boilers. This "fur" consists chiefly of chalk, which dissolves slightly in water containing carbon dioxide, though it is almost insoluble in pure water. Consequently when the carbon dioxide is driven off by boiling, the chalk separates out. Cavendish also showed that waters which owe their "hardness" to the presence of chalk can be "softened" by adding lime, which removes the carbon dioxide dissolved in the water by combining with it to form chalk. After the water has been deprived in this way of the carbon dioxide, the chalk which was originally in solution separates out. Cavendish also weighed a bladder filled with common air and then with "fixed air," and found the latter to be one and a half times heavier than the former.

Chemists living before the 18th century knew that an inflammable gas is evolved when certain metals are brought in contact with acids, but Cavendish was the first (1766) to accurately describe the properties of this gas (hydrogen) under the title "inflammable air." He prepared it by dissolving iron, zinc, or tin, in muriatic acid (hydrochloric acid). Though a highly inflammable gas, he showed that it could not burn unless supplied with common air. He also weighed bladders of hydrogen and common air to determine their relative weights.

"Inflammable air" was considered by the chemists of that day to be pure phlogiston. Cavendish himself held this opinion at first, but afterwards regarded the gas as phlogisticated water.

Cavendish appears to have had an inordinate desire to weigh and measure everything he came across, and the accuracy of his results are perfectly marvellous considering the apparatus at his disposal. He determined the mean composition of the air, and gave as his result in 100 parts by volume

Oxygen—20·8
Nitrogen—79·2

Bunsen (1811-1899) who was an extremely accurate worker, and brought gas analysis to a remarkable degree of perfection, obtained as the mean of twenty-eight analyses

Composition of air in 100 parts by volume
Oxygen—20·9
Nitrogen—79·1

a result agreeing very closely with that obtained by the earlier chemist.

Cavendish compared the weight of the earth with that of a globe of water of the same size, and concluded that the earth was about five and a half times the heavier.

Cavendish noticed that common air is frequently diminished in volume when substances burn in it, and Priestley had drawn attention to the fact that moisture is formed when common air and "inflammable air" are exploded by the electric spark in a dry glass vessel. Cavendish repeated this experiment many times with varying but known quantities of "inflammable air" and common air, and noted the diminution of volume caused by the explosion and also the volume of oxygen left. He found that the greatest diminution of volume occurred when 2 vols of "inflammable air" (hydrogen) were mixed with 5 vols of common air. It is interesting to read the account of this experiment in Cavendish's own words:

"The better to examine the nature of the dew, 500,000 grain measures of inflammable air were burnt with about 2½ times that quantity of common air, and the burnt air made to pass through a glass cylinder eight feet long and three-quarters of an inch in diameter, in order to deposit the dew. By this means upwards of 135 grains of water were condensed in the cylinder, which had no taste or smell, and which left no sensible sediment when evaporated to dryness; neither did it yield any pungent smell during the evaporation; in short, it seemed pure water."

Cavendish afterwards performed similar experiments using dephlogisticated air (oxygen) instead of common air, and he gives the following account of one of these experiments.

"I took a glass globe holding 88,000 grain measures, furnished with a brass cock, and an apparatus for firing air by electricity. This globe was exhausted by an air-pump and then filled with a mixture of inflammable and dephlogisticated air by shutting the cock, fastening a bent glass tube to its mouth, and letting up the end of it into a glass jar, inverted in water, and containing a mixture of 19,500 grain measures of dephlogisticated air, and 37,000 of inflammable; so that on opening the cock some of this mixed air rushed through the bent tube and filled the globe. The cock was then shut, and the included air fired by electricity, by which means almost all of it lost its elasticity. The cock was then again opened, so as to let in more of the same air, to supply the place of that destroyed by the explosion, which was again fired, and the operation continued till almost the whole of the mixture was let into the globe and exploded. By this means, though the globe held not more than the sixth part of the mixture, almost the whole of it was exploded in it, without any fresh exhaustion of the globe."

Cavendish concluded from his experiments that "there seems the utmost reason to think that dephlogisticated air is only water deprived of its phlogiston, and that inflammable air . . . is either phlogisticated water, or else pure phlogiston; but in all probability the former." So although Cavendish really proved that pure water consists of hydrogen and oxygen in the proportion of two volumes of the former to one of the latter, being misled by the phlogiston theory he failed to grasp the full significance of his results, and it was left for Lavoisier in 1783 to give a clear explanation of the composition of water.

To Cavendish also belongs the honour of elucidating the composition of nitric acid (aquafortis). Instructions how to prepare this acid by strongly heating a mixture of saltpetre, alum, and sulphate of copper, are given in a Latin translation of the works of Geber, an Arabian alchemist of the 8th century.

Priestley had observed that an acid is formed when the electric spark is passed through moist atmospheric air, and Cavendish noticed that the water prepared from inflammable air (hydrogen) and dephlogisticated air (oxygen) was sometimes acid in taste, and when saturated with alkali and evaporated it gave nitre. As the result of a series of careful experiments he found that this formation of acid was due to the presence of traces of phlogisticated air (nitrogen) and that when more phlogisticated air was intentionally added a larger quantity of acid was formed.

It is interesting to note that Cavendish was the first chemist to dry gases, and to use mercury for collecting those soluble in water.

JOSEPH PRIESTLEY

1733-1804

JOSEPH PRIESTLEY, the son of a cloth-dresser, was born at Fieldhead, near Leeds, 1733. His mother died when he was seven years old, and he was brought up by a sister of his father who had a comfortable income. Joseph was a delicate child and his early education was irregular, so it was fortunate for him that his aunt's house was much frequented by dissenting ministers of all denominations, as in this way he came in contact with many cultured men, and acquired much useful information by listening to their conversation.

Brought up amidst such surroundings, it is not surprising that Priestley chose the ministry for his profession. He entered the Dissenting Academy at Daventry when he was nineteen years old. At this time he had a fair knowledge of several languages, and also knew a little geometry, mathematics and natural philosophy. Joseph spent three happy years here, and left to become assistant minister at Needham Market, Suffolk. His start in life was not very encouraging. He had an impediment in his speech and this, joined to his peculiar theological views, made his congregation rapidly decrease. He tried to add to his income by teaching, but failed.

After three years he went to Nantwich in Cheshire, where most of his time was employed in teaching. He was much more successful here, and in 1761 was appointed "tutor in the languages" in a newly established Dissenting Academy at Warrington. He stayed here till 1767, and during this time made the acquaintance of Dr. Benjamin Franklin, who stimulated Priestley's interest in natural philosophy, and later on fostered his desire to write a "History of Electricity," and lent him books bearing on the subject. Priestley gave an account of many original observations in his History, and the book attracted the attention of scientists. The author was elected a Fellow of the Royal Society and made a Doctor of Laws of Edinburgh University.

Priestley married during his stay at Warrington, and in 1767 removed with his wife and family to Leeds, where he remained for several years as minister of Millhill Chapel. In 1772 he accepted the post of "literary companion" to Lord Shelburne, and while in his employ went to Holland, Germany and Paris. His duties were very light, and he was able to give nearly all his time to chemical research. He left Lord Shelburne in 1779 and again took up the work of the ministry in Birmingham.

Priestley had somewhat socialistic opinions, sympathized with the French Revolutionists, and was an open enemy of the Church of England. Some of his friends in 1791 celebrated the anniversary of the taking of the Bastile by a public dinner. This roused the fury of the populace, and a mob collected and destroyed the dissenters' chapels and houses, and although Priestley was not present at the dinner his house was burnt, and his apparatus, manuscripts and library destroyed. He fled to London and became minister to a congregation at Hackney; but tradespeople were afraid to have his custom, and many scientists refused to acknowledge him, so at the end of three years he followed his sons to America and died at Northumberland, a little town on the Susquehanna, in 1804.

The Royal Society awarded him the Copley medal in 1733.

When Priestley went to Leeds he happened to live near a brewery, where fixed air is produced in large quantities during the process of fermentation. Although at this time he had scarcely any knowledge of chemistry, he had read of Black's experiments with "fixed air" and, as it was easy for him to procure some, Priestley thought he would examine its properties himself. He became so interested in this "air" that he continued his investigation of it even after he left the neighbourhood of the brewery and invented the well-known pneumatic trough, to collect and preserve the gas, which he had now to prepare for himself from chalk. He discovered that "fixed air" gives a very pleasant taste to water, and in 1772 he published a pamphlet on this subject, entitled: "Impregnating Water with Fixed Air," to which the manufacture of soda-water owes its origin.

Priestley also studied "inflammable air" (hydrogen). Phlogiston was generally supposed to be a solid, earthy, volatile substance, in accordance with Stahl's doctrine, until Cavendish discovered "inflammable air," and suggested that this new "air" might be the mysterious principle phlogiston. Metals were thought to consist of an earthy powder—the calx—and phlogiston. When a metal was burnt the phlogiston rushed out causing the phenomena of heat and light, and the calx (really oxide) of the metal remained, so it followed that if phlogiston could be restored to the calx of any metal, that particular metal would be regenerated, and Priestley argued if metals could be produced from their corresponding calxes by "inflammable air" then this "air" must be phlogiston.

He put some calx of lead (minium) into a cylinder filled with inflammable air inverted over water, and heated the calx with a burning lens. It is extremely interesting to read his quaintly expressed account of the experiment.

"As soon as the minium was dry, by means of the heat thrown upon it, I observed that it became black, and then ran in the form of perfect lead; at the same time that the air diminished at a great rate, the water ascending within the reciever, I viewed this process with the most eager and pleasing expectation of the result, having at that time no fixed opinion on the subject ; and therefore I could not tell except by actual trial whether the air was decomposing in the process, so that some other kind of air would be left, or whether it would be absorbed in toto. . . . Seeing the metal to be actually revived, and that in a considerable quantity, at the same time that the air was diminished, I could not doubt but that the calx was actually inbibing something from the air ; and from its effects in making the calx into metal, it could be no other than that to which chemists had unanimously given the name of *phlogiston.*"

He performed many similar experiments, using the calxes of different metals, sometimes inverting the cylinder over quicksilver instead of water, and found that in every case the inflammable air was totally absorbed. Hence he concluded "that phlogiston is the same thing as inflammable air, and is contained in a combined state in metals, just as fixed air is contained in chalk and other calcareous substances : both being equally capable of being expelled again in the form of air."

When Cavendish was conducting his investigation on "inflammable air" he noticed that an incombustible "air" is given off when iron and other metals are dissolved in nitric acid, or aqua fortis, as it was then called.

Priestley, who was never so happy as when investigating a fresh "air," determined to study this one. He obtained it readily by the action of nitric acid on copper, and called it "nitrous air." He found that when mixed with common air there was a diminution of volume accompanied by evolution of heat and formation of red fumes. He noted that not the whole of a given volume of common air, but only one fourth part of it, was capable of being "devoured" by nitrous air, and also that only air "fit for respiration" gave these phenomena. The compound of "vital air" and "nitrous air" is soluble in water, and he devised an apparatus for comparing the quantities of "vital air" in the atmosphere and other mixtures of "airs" by measuring what proportion of the original air could be "devoured" by nitrous air, and then removed from the residual air by dissolving in water.

Although Priestley's apparatus or eudiometer passed into common use, it did not give very accurate results.

Cavendish tried to prepare "inflammable air" by acting on copper with spirit of salt or "marine acid," but instead of hydrogen he obtained an air that "lost its elasticity by coming in contact with water." Priestley (1772) collected some of this "air" over quicksilver and found that the copper did not enter into the reaction, as the "air" was evolved just as readily when the acid was heated by itself. He called the gas "marine acid air" and noted that it was not condensed by the application of cold.

In 1775 Priestley heated oil of vitriol (sulphuric acid) in the hope of obtaining an "acid air" from it. He applied heat for a long time, but was disappointed in his expectations, and proceeded to disconnect his apparatus; while doing so, a little mercury came in contact with the hot acid. There was a violent reaction which broke the vessel containing the acid, and Priestley was badly burnt. Nothing daunted, however, he heated a fresh supply of acid with a small quantity of mercury and so obtained, "vitriolic acid air," now called sulphur dioxide.

Scheele discovered silicon tetrafluoride in 1771, but Priestley also prepared it by heating fluor spar with oil of vitriol in a glass vessel. He called it "fluor acid air," and showed that it gives a gelatinous precipitate when conducted into water (silicic acid).

Priestley was the first to obtain ammonia in the form of a gas, and called it "alkaline air." He passed electric sparks through it, and showed that the "air" increased in volume and was decomposed into "inflammable air" and "phlogisticated air." He tried the effect of mixing "alkaline air" (ammonia gas) with "marine acid air" (hydrochloric acid gas) and so obtained sal ammoniac.

This chemist discovered "nitrous oxide air," a gas used in dentistry to produce insensibility while teeth are extracted, and in 1800 showed that carbonic oxide consists only of carbon and oxygen.

By far the most important air Priestley discovered was oxygen. On August 1st, 1774, he was amusing himself by observing the action of heat on various substances, by means of a burning glass, (*e.g.* a lens capable of concentrating the sun's rays) when he obtained from red precipitate (oxide of mercury) an air in which a candle burnt with a "remarkably vigorous flame;" he found by experiment that this air had "all the properties of common air, only in much greater perfection," and called it "deplogisticated air." He found later that the same air could be obtained from red lead, manganese oxide, etc., by the action of heat, and from various other salts by the action of acids. He gave an account of oxygen in "Experiments and Observations on different kinds of air," published in 1775.

Priestley recognised that combustion proceeded better in this gas than in any other, and assumed further that atmospheric air owes its property of supporting combustion and respiration to the presence in it of this "air." He showed that common air, which has been rendered "noxious" by the burning of a candle, by respiration, or by putrefaction, could be restored to its original state by the action of growing plants. He also found that oxygen is absorbed by nitric oxide.

The Phlogiston Theory was already tottering to its fall, and the discovery of oxygen was the veritable "last straw," though Priestley refused to recognise it, and remained its faithful champion until his death.

CARL WILHELM SCHEELE

1742-1786

Carl Wilhelm Scheele was born December 9th, 1742, at Stralsund, where his father was a merchant.

He was educated first at a private and afterwards at a public school in his native town. When he was fourteen years old he was apprenticed to Bauch, an apothecary in Gothenburg. His master had a fair chemical library, and Carl would often sit up at night studying such works as Lémery's "Cours de Chimie" or performing experiments taken from Neumann's "Chymie."

In 1765 he went to an apothecary at Malmo, and in 1768 to Stockholm. In 1773 he obtained work in a pharmacy at Upsala, and while there he made the acquaintance of Bergmann, who afterwards became his close friend and patron.

In 1776 he was appointed *provisor* of the pharmacy at Köping. He hailed the appointment with delight as promising a competency and leisure for his beloved experiments. He once wrote, "There is no delight like that which springs from a discovery. It is a joy that gladdens the heart," but his hopes were bitterly disappointed, and poverty and hardship were his portion for many years. However, he manfully struggled against adverse circumstances, and by 1782 had improved his position so much that he was able to build himself a good laboratory. But the years of privation had undermined his health, and he died at Köping, 21st May, 1786, at the early age of forty-four.

Scheele was an adherent of the Phlogiston Theory, but his views were somewhat peculiar, as he seems to have ascribed to phlogiston properties similar to those of the ether of physicists. He regarded hydrogen as composed of phlogiston and "matter of heat."

Although Scheele died at a comparatively early age he discovered a very large number of new substances, more perhaps than any other investigator except Priestley.

Pyrolusite was known to the ancients, who thought it was an ore of iron. Pott, in 1740, showed that it did not contain iron. In 1774 Scheele published his celebrated investigation on this mineral, and expressed the opinion that pyrolusite is a metallic calx. He found a new earth in a specimen of this ore he was examining (baryta), and showed that it gives a salt, insoluble in water, on treatment with sulphuric acid ($BaSO_4$). He found that this salt can be rendered soluble by ignition with carbon and an alkali. Chlorine is another new substance he came across in the course of this investigation. He found this gas was evolved on treating manganese dioxide with marine acid (hydrochloric acid). He called it "dephlogisticated marine acid gas," that is marine acid (hydrochloric acid) deprived of its phlogiston (hydrogen). Scheele found that chlorine has bleaching properties.

Oxygen was discovered independently by two chemists, Priestley and Scheele.

Scheele prepared the gas by distilling a mixture of manganese dioxide and arsenic acid; by acting on potassium nitrate with sulphuric acid, and in many other ways.

Gahn, in 1769, found that bones contain calcium phosphate, but Scheele, in 1775, was the first to prepare phosphorus from this source, and his method is almost identical with that still used. He warmed bone-ash for several days with dilute nitric acid, then added sulphuric acid to precipitate the calcium as sulphate. He allowed this sparingly soluble salt to settle, then poured off the liquid and evaporated it to a syrup, mixed it with charcoal, and distilled.

During the course of his examination of Prussian blue, Scheele discovered hydrocyanic acid (1782), and was the first to prepare arsenic acid by dissolving arsenious oxide in aqua regia. In 1775 he obtained arseniuretted hydrogen by treating a solution of arsenic acid with zinc, and a compound of copper and arsenic ($CuH\ AsO_3$ cupric arsenite) by precipitating a solution of potassium arsenite with copper sulphate. This substance is used as a pigment under the name of Scheele's Green.

Sulphuretted hydrogen was known in the sixteenth century as a "sulphurous vapour," but Scheele was the first chemist to investigate this gas. He prepared it by heating sulphur in "inflammable air," (hydrogen) and therefore concluded that it must consist of sulphur, phlogiston, and a "matter of heat." It will be remembered that he looked upon "inflammable air" (hydrogen) as a compound of phlogiston and "matter of heat."

Scheele also investigated fluor spar, and stated that it was the calcium salt of a new acid which he obtained in an impure state by distilling fluor spar with sulphuric acid in a tin retort:

$$CaF_2 + H_2SO_4 = 2HF + CaSO_4$$

by acting with this new acid on silica he prepared silicon tetrafluoride (SiF_4).

Graphite and sulphide of molybdenum (MoS_2) were both known to the ancients, and the names plumbago and molybdaena were applied indiscriminately to either substance. Scheele showed (1778) that molybdaena gives sulphuric acid when treated with nitric acid, an acid oxide remaining behind, and hence concluded that the mineral was a compound of this acid and sulphur, while plumbago (1779), when treated with nitric acid, gives off "fixed air" (carbon dioxide) and therefore must be a kind of mineral carbon. In 1781 he proved that tungsten (calcium tungstate) is composed of lime, combined with a peculiar acid.

Scheele made investigations on the nature of microcosmic salt and borax, and invented fresh methods of preparing calomel, powder of algaroth, magnesia alba and ether. He discovered ferrous amonium sulphate, and was the first chemist to find out and use distinctive reactions for the detection and separation of similar substances, thus laying the foundation of qualitative analysis.

Nitrogen was discovered by Dr. Rutherford in 1772, but Scheele was an independent discoverer of this gas, and showed that it is present in ammonia.

In addition to all these discoveries, this indefatigable worker enriched organic chemistry with many new substances. He was the first to prepare glycerine from olive oil and lead oxide. He discovered mucic and pyrogallic acids, also lactic acid in sour milk, gallic acid in nut galls, oxalic acid in wood sorrel, and prepared this acid artificially by the action of nitric acid on cane sugar, which has remained the standard laboratory method of preparing the acid to this day.

He prepared mallic acid from apples, citric acid from lemons, uric acid from urine, tartaric acid from grapes. He did not discover benzoic acid, but showed that it could be obtained in a pure form by boiling gum benzoin with milk of lime, filtering, and precipitating the benzoic acid with hydrochloric acid.

Scheele's greatest work was "Chemical Observations and Experiments on Air and Fire." Most of the experiments described were done from 1770-1773, and the manuscript was sent to the publisher in 1775, but the book was not printed until 1777. This unfortunate delay lost Scheele the credit of the discovery of oxygen and nitrogen, and it is only recently that his claims have been recognised. In this book he treats of metallic calxes and combustion, makes many interesting observations on the nature of radiant heat, and describes experiments on the composition of the atmosphere.

Scheele tried to find out what part air takes in the phenomenon of combustion.

He introduced different substances supposed to contain phlogiston into a measured volume of air ; a solution of an alkaline sulphide, moist iron filing, etc., and observed that the air gradually became smaller in volume, and would no longer support combustion. He noted that the residual air was lighter than common air, and concluded that " air must be composed of two different kinds of elastic fluids." He next burnt phosphorus metals, etc., in a measured volume of air, with a view to ascertaining what became of the portion of the air that disappeared, and came to the conclusion that it combined with the phlogiston of the combustible substance, and escaped as heat through the glass. He appears to have thought heat a compound of fire-air (oxygen) and phlogiston. He found that calx of mercury (red oxide of mercury), gave fire-air (oxygen) and mercury when heated. Now metals were supposed to consist of their calxes and phlogiston,

$$\text{heat} + \text{calx of mercury gave mercury} + \text{fire air,}$$

that is

$$\text{heat} + \text{calx of mercury} = \overbrace{\text{calx of mercury} + \text{phlogiston}} + \text{fire air};$$

cross out calx of mercury from each side of the equation and

$$\text{heat} = \text{phlogiston} + \text{fire air}$$

remains.

This book was much in request, and was translated into various European languages.

The Phlogiston Theory has long since passed away, and Scheele's mistaken views on combustion are almost forgotten, but his experiments and discoveries are remembered and will always excite admiration, the more so as they were the work of a man hampered by poverty and a meagre education.

ANTOINE LAURENT LAVOISIER

1743-1794

Antoine Laurent Lavoisier, the son of a wealthy advocate, was born in Paris, 1743. He received an excellent education at the Collège Mazarin, and studied physics, astronomy, botany and chemistry. Early in life he thought of making the Law his profession, but he soon abandoned the idea and resolved to devote himself to the study of Natural Science, and in 1768 he was admitted to the Académie des Sciences.

Although Lavoisier had inherited a considerable sum of money from his mother, he did not find it sufficient to carry out all his Scientific projects, and in order to increase his income he became a fermier-général or tax-collector, under the Government in 1769. In 1775 he was appointed one of four commissioners entrusted with the manufacture of the gunpowder used by the State, and he simplified the method of production, and increased the efficiency of this substance. In 1785 he became a member of the Committee of Agriculture, and did much to improve this industry and to ameliorate the condition of the peasants. In 1791 he was appointed Secretary and Treasurer of the Commission of Weights and Measures, whose aim was to supply the world with an international system based upon a natural unit.

Lavoisier freely gave both time and money, and worked hard to promote the welfare of his country and to further Science, but all this counted for nothing in the eyes of the Revolutionists, and on May 8th, 1794, twenty-eight Fermiers-Généraux, including Lavoisier, were brought to trial and condemned to death, and the sentence was carried out the next day.

As early as 1764 Lavoisier evinced his scientific ability by winning a prize offered by the French Government for an essay giving the best method of lighting the streets of a large town. It is worth mentioning, as showing Lavoisier's thoroughness and unselfish devotion to science, that for six weeks he deprived himself of daylight, and lived in rooms lighted only by artificial light, in order to train his eyes to judge of the value of different illuminants.

It was commonly supposed that water could be converted into earth by means of heat, as earthy matter makes its appearance when water is boiled for some time in a glass vessel, but in 1770 Lavoisier gave the true explanation of this phenomenon. He distilled water for 101 days in a glass vessel closed with a glass stopper and furnished with a glass tube connecting the neck with the body of the vessel so that the steam was condensed and flowed back into the original receptacle. He weighed the apparatus empty, and again after he had put some water in it. Earthy matter was formed at the end of a month, and after 101 days he judged the quantity to be sufficient for his experiment. He again weighed the apparatus and found the total weight of vessel, water and earthy matter, the same as that of the vessel and water before heating. He poured out the water, evaporated it to dryness, and found the weight of the residue to be 20.4 grains. He then weighed the empty vessel, and found its weight 17.4 grains less than before heating; hence he concluded that the water had not been changed into earth, but had acted upon and dissolved a portion of the glass. It is true the glass vessel had only lost 17.4 grains, and the water had gained 20.4 grains, but he boldly asserted that the 3 grains difference was due to experimental error—an explanation that all subsequent investigation has shown to be the true one.

Scheele also made the alleged conversion of water into earth the subject of experiment. He analysed the earth and found it to consist of the same substances as the glass, and hence came to the same conclusion as Lavoisier.

Hooke and Mayow had noticed that substances are heavier after combustion than before, and Mayow gave the true explanation of combustion, viz.: that it consists in the union of the body burnt with the "nitro-aerial spirit" of the air, causing increase of weight. But Mayow's correct view was disregarded and Stahl's Phlogiston Theory of Combustion was generally accepted, until Lavoisier enunciated his oxidation theory.

In 1772 Lavoisier handed in to the Academy a sealed paper, opened on the first of May, 1773. In it he stated that sulphur and phosphorus when burnt gain in weight instead of losing it, and showed that this gain is due to absorption of air. In 1774 he gave a resumé of his work "On the Calcination of Tin." The method he adopted for the calcination of tin was as follows :—

A weighed quantity of tin was put in a glass retort and heated to melting, the end of the retort was then sealed up at the blowpipe, the whole allowed to cool, and weighed. The tin was again heated to its melting point and kept for some time at this temperature. When cool the retort (still sealed up) was weighed : the weight was the same as before heating. The sealed end was then broken off, air rushed in. The retort and contents were once more weighed : the weight was now greater than before. The calx of tin was next removed from the retort and weighed. The calx weighed more than the tin originally put in the retort, the increase in weight being approximately equal to the increase in weight of the retort and contents after air had been admitted ; hence Lavoisier concluded that the formation of calx of tin was due to absorption of air, and that the difference in weight between the tin and calx of tin was equal to the weight of air absorbed in its formation. He adds that probably air consists of two or more constituents, and that probably only one of them united with the tin.

In 1774 Priestley visited Paris and was present at a dinner party given by Lavoisier. During the evening Priestley gave an account of his discovery of an "air" (dephlogisticated air) which he had obtained from red oxide of mercury and also from red lead.

Lavoisier quickly realised the importance of this new gas, and gave an account of its preparation and properties in a paper (1775) "On the Nature of the Principle which combines with the Metals during their Calcination, and which augments their Weight."

During the next few years Lavoisier continued his researches on air and combustion, and made his classical experiment on red-oxide of mercury.

He put four ounces of mercury in contact with 50 cubic inches of air, and heated the mercury to nearly its boiling point for twelve days; it became covered with red specks of oxide of mercury. He noted that between 7 and 8 cubic inches of air had disappeared, and found that the residual gas was nitrogen. He then weighed the oxide of mercury formed ; its weight was 45 grains. He next heated this 45 grains of red oxide of mercury in a small retort, and collected the gas given off; its volume was between 7 and 8 cubic inches, and it consisted of oxygen ; 41½ grains of metallic mercury remained in the retort.

Lavoisier also burnt phosphorus in a confined volume of air, and found that the sides of the vessel became covered with a white powder which he named phosphoric acid. He noticed that about one-fourth of the air disappeared, and that the remainder (nitrogen) would not support combustion or respiration, so he named it *azote* from two Greek words meaning "life" and "privative."

Although Lavoisier was firmly convinced that phlogiston does not escape during combustion, he could not entirely silence the followers of Stahl. They asked "Why are the metals regenerated on heating their calxes with inflammable air? Why is inflammable air evolved, and why are calxes of the metals produced when metals are dissolved in dilute acid? *We* say a metal consists of its calx and phlogiston. Inflammable air is phlogiston, therefore when a calx absorbs inflammable air the metal is regenerated. Similarly, when a metal is dissolved in a dilute acid, the acid causes the metal to give up its phlogiston, and the calx remains. What answer can *you* give to these questions?"

Lavoisier had to confess he could give no answer at all. But in 1783 he heard that Cavendish had obtained water by exploding a mixture of dephlogisticated and inflammable airs, and this gave him the key to the mystery.

Lavoisier repeated Cavendish's experiment and also obtained water. Subsequently he passed steam over red-hot iron filings, and showed that the steam was thereby decomposed into oxygen which united with the iron, giving calx of iron (oxide of iron) and inflammable air (hydrogen) which was evolved.

Lavoisier could now give answers to the questions propounded by the holders of the Phlogiston Theory.

When inflammable air acts on the calx of a metal it abstracts oxygen from the calx to form water, and the metal is regenerated. When a metal dissolves in a dilute acid, the water in the acid (according to Lavoisier) is decomposed by the metal, inflammable air is evolved, and the remaining dephlogisticated air unites with the metal to form a calx, which then dissolves in the acid.

Priestley, and also Scheele, discovered oxygen, and Cavendish synthesised water, but these chemists were followers of Stahl, and were quite satisfied to explain their results in accordance with his teaching. Other chemists noticed that metals increase in weight on combustion, and rejected the doctrine that phlogiston is "the principle of levity," and Mayow gave the true explanation of combustion but no one heeded him. It was Lavoisier, and Lavoisier alone who overthrew the Phlogiston Theory, and evolved the new theory of oxidation. His reputation and high position in the Scientific world secured attentive consideration for his views, and the careful experiments on which his theory was based and the clear way in which he presented it, soon won many adherents. It is greatly to be deplored that Lavoisier tried to claim the credit of discovering oxygen and the synthesis of water. Honour and admiration are justly due to him for his correct interpretation of these discoveries, but his fame has been dimmed and not enhanced by the attempt to appropriate the work of others.

Ladenburg gives the following summary of Lavoisier's theory of combustion :

1. "In all chemical reactions it is the kind of matter alone that is changed, whilst its quantity remains constant ; consequently, the substances employed and the products obtained may be represented by an algebraic equation in which, if there is any unknown term, this may be calculated.

2. In the process of combustion the burning substance unites with oxygen, whereby an acid is usually produced. In the combustion of the metals, metallic calxes are produced.

3. All acids contain oxygen, united, as he expresses it, with a basis or radical which, in inorganic substances, is usually an element, but in organic substances is composed of carbon and hydrogen, and frequently contains also nitrogen or phosphorus."

This chemist was the first to grasp the principle of the indestructibility of matter, and asserted that in chemical reactions the *quantity* of matter remains constant, only the *form* is changed, and therefore chemical reactions can be expressed by algebraic equations.

He thought that all acids contain oxygen (a mistake corrected by Davy) united with a basis or radical, which in inorganic substances is usually an element, but in organic substances is usually a compound of carbon and hydrogen, and sometimes of nitrogen or phosphorus as well.

Black found that "fixed air" (carbon dioxide) is formed when charcoal is burnt, and Lavoisier made further researches on this subject.

He put a known weight of charcoal in a dish, together with a trace of phosphorus and tinder. He put the dish under a bell-jar filled with oxygen, standing over mercury, and ignited the tinder and phosphorus with a red-hot wire, thus setting fire to the charcoal. When the charcoal had ceased burning he weighed what remained, and measured the volume of oxygen left in the bell-jar. He then absorbed the "fixed air" (carbon-dioxide) formed by means of potash, and read the volume of oxygen left. He knew the weight of charcoal burnt, the volume of oxygen used, and the volume of "fixed air" formed, and so calculated its composition. He gave as his result that about 70 parts by weight of oxygen combine with about 30 parts by weight of charcoal.

Lavoisier showed that charcoal and diamond both consist of carbon by making a similar experiment to the one just described, but substituting a diamond for charcoal, and a burning glass for the phosphorus, tinder, and hot wire.

Lavoisier was now in a position to find the quantitative composition of certain organic bodies consisting of carbon, hydrogen and oxygen. He burnt substances such as spirit of wine, oil, wax, in oxygen, under a graduated bell-jar, and measured the volume of oxygen consumed and the volume of carbon-dioxide produced and calculated the percentage composition of the substance investigated. This was the first attempt at organic analysis.

Priestley studied respiration and showed that plants purify the air. Lavoisier extended his investigations and showed that respiration is analogous to combustion. He also did good work in conjunction with Guyton, Berthollet and Fourcroy, in revising chemical nomenclature.

On the whole, Lavoisier had very sound ideas about heat, though he speaks of a "matière du feu." He had the modern conception that matter consists of small particles, but thought that "matter of heat" exists between the particles. He speaks of it as "a very subtle fluid, which insinuating itself between the particles of bodies separates them from each other." Later, he employed the term *caloric* instead of "matter of heat." In conjunction with Laplace he determined the specific heats of iron, mercury, etc., by means of an ice calorimeter.

In 1789 he brought out his "Elemens de Chimie," which gives a full account of his theoretical views and the experiments on which they were based.

Professor Brande says of Lavoisier :

"As a theorist, he has few equals ; he was comprehensive, successful and clear." Further, "Contemporary historians agree in eulogizing his mild, amiable and obliging manners, in extolling his liberality, and in praising him as the encourager of deserving ingenuity and the ardent patron of science and the arts."

CLAUD LOUIS BERTHOLLET

1748-1822

Claud Louis Berthollet was born at Talloire in Savoy, 1748. He was educated at Chambéry and at the Collège des Provinces at Turin, where he gained a medical degree in 1768.

He went to Paris in 1772, and was appointed physician to the Duke of Orleans. In 1781 he was elected a member of the Academy of Sciences, and a few years afterwards was appointed Government Commissary and Superintendent of dyeing processes. He wrote a book on the theory and practice of this art, which was better than any that had been previously written.

During the Revolution, Berthollet travelled about France, teaching how to extract and purify Saltpetre required for the manufacture of gunpowder, and also how to prepare steel, In 1794 he was appointed Professor of Chemistry at the Polytechnic and Normal Schools, and soon afterwards was sent to Italy. He met Bonaparte there, accompanied him to Egypt, and did good scientific work in that country.

Berthollet possessed both moral and personal courage, and on one occasion defied the Committee of Public Safety itself. He was requested to analyse some brandy and to find poison in it, to serve as a pretext for the execution of certain persons whom Robespierre wished to get rid of. The chemist performed the analysis, but found no poison, only small particles of slate removable by filtration, and he gave a report to this effect.

The Committee of Public Safety was furious at having its plans upset in this way, and sent for Berthollet to try to persuade him to alter his report, but he refused, and declared his analysis correct, and to prove it, filtered a glass of the suspected brandy in the presence of the Committee, and boldly drank it off. His life would have paid the penalty, but fortunately he was too useful to be dispensed with.

Berthollet became a senator under the first

Consul, and subsequently Napoleon made him a Grand Officer of the Legion of Honour and a Count.

After the restoration, Louis XVIII. created him a peer. It will interest all those who have an affection for the canine tribe to know that he chose as his armorial-bearing, the figure of his faithful dog!

In 1822 the chemist had a fever, followed by boils and a very painful gangrenous ulcer, of which he died in the same year.

Several attempts were made during the phlogiston period to secure a uniform systematic chemical nomenclature, but they all ended in failure. In 1782 Guyton de Morveau laid before the French Academy a system that had much in its favour, but since it was based on the phlogistic theory—a theory already tottering to its fall—it was not accepted by the leading French chemists.

In 1787 Guyton became a convert to the new theory of combustion, and assisted by Lavoisier, Barthollet, and Fourcroy, drew up a Nomenclature Chimique which is the basis of that we now employ.

Lavoisier's antiphlogistic theory found a firm supporter in Berthollet, who was the first French chemist of note to declare his belief in the new doctrine, but he did not agree with Lavoisier's statement that oxygen enters into the composition of all acids, and showed that both prussic acid and sulphurretted hydrogen have acid properties and yet contain no oxygen. Berthollet's views, though disregarded in his own day, are now universally acknowledged to have been correct.

Scheele discovered chlorine in 1774. He prepared it by the action of marine acid (hydrochloric acid) on manganese ore, and called it "dephlogisticated marine acid gas." Berthollet, in 1785, read a paper on this gas before the Academy of Sciences, and it may be remarked in passing that it was on this occasion that he announced his disbelief in phlogiston.

Berthollet found that water impregnated with Scheele's gas lost its green colour when exposed to light, gave out oxygen, and became marine acid. Hence he thought that chlorine, as this gas is now called, is formed by the union of marine acid and oxygen. He described other experiments he had made, which supported this view, including the following: "I calcined some manganese at a strong heat, and extracted from it a large quantity of vital air (oxygen); it lost one-eighth of its weight. In this state I treated it with marine acid, and obtained from it a much smaller quantity of dephlogisticated marine acid. The formation of dephlogisticated marine acid is due, therefore, to the vital air of the manganese which combines with the marine acid."

The following equations show the modern interpretation of Berthollet's results.

$$\begin{array}{lcl}
3\,MnO_2 & = & Mn_3O_4 + O_2 \\
\text{manganese dioxide} & & \text{manganous-manganic oxide} \\
MnO_2 + 4HCl & = & MnCl_2 + 2H_2O + Cl_2 \\
Mn_3O_4 + 8HCl & = & 3MnCl_2 + 4H_2O + Cl_2
\end{array}$$

Although subsequent investigators have shown that Berthollet was mistaken in the composition of this substance he considerably added to the knowledge of its properties, and he was the first to demonstrate that chlorine can be used as a bleaching agent.

When the Nomenclature Chimique was drawn up in 1787, the name of dephlogisticated marine acid was changed to oxygenated muriatic acid (afterwards shortened into oxymuriatic acid) to show the supposed relation of this gas to muriatic acid (marine acid).

Priestley was the first chemist to obtain ammonia as a gas; he called it "alkaline air," and noticed that its volume underwent a remarkable change when he passed electric sparks through it. Berthollet advanced a step further and showed that the sparks had decomposed ammonia into hydrogen and azote (nitrogen). He also discovered silver fulminate, and was the first to obtain pure potassium hydroxide, by dissolving the crude product in alcohol.

Chemists, up to the beginning of the nineteenth century, considered it a self-evident fact that substances combine in fixed proportions, but in 1803 Berthollet brought out his "Statique Chimique," in which he denied the constancy of chemical proportions, and supported his view by arguments and experiments.

The book was mainly directed against the false views of affinities then in vogue, and against the misuse of tables of affinity. The earliest of these tables was complied by Geoffroy, 1718. The affinity of one substance towards another was considered invariable till 1773, when Beaumé showed that affinities are different at ordinary and high temperatures ; so Bergman drew up two tables of affinities, one for ordinary and the other for very high temperatures. He arranged his tables in this way: He took a given substance A, and put 58 other substances, capable of combining with it, in order 1, 2, 3, &c., so that 1 decomposed the substance formed by the union of A and 2, 2 decomposed the substance formed by the union of A and 3, and so on throughout the list.

These tables were considered very useful and important, and were universally accepted as correct until Berthollet attacked them in his book, and asserted that the action of one substance on another is not fixed and invariable but depends upon the mass of each present, and also on the condensation, which is affected by physical conditions (pressure, temperature, etc.)

According to Berthollet the state of condensation of any substance depends upon two opposite forces, cohesion and elasticity. When the cohesion is greater than the elasticity the substance is solid, when the cohesion is less than the elasticity the substance is a gas, and when the cohesion and elasticity just balance the substance is liquid.

He also states that when an acid is added to a salt in solution, the base is shared between the two acids in the ratio of their affinities :

$$\frac{\text{constant}}{\begin{array}{c}\text{quantity of acid which neutralises}\\ \text{unit weight of alkali}\end{array}}$$

or according to the "masse chimique," as he terms it. For example, if a solution of potassium nitrate be mixed with a solution of sulphuric acid, the solution contains both potassium nitrate and potassium sulphate. If, however, one salt is quite insoluble, we get complete precipitation, *e.g.*, barium sulphate is precipitated by sulphuric acid from a barium nitrate solution, because the barium sulphate, owing to its insolubility, is continually removed from the reaction. Similarly, when a volatile substance is formed, as carbon dioxide, the decomposition proceeds to the end.

Berthollet's ideas with regard to precipitation and gas evolution can be traced in modern works on Chemistry, as also his theory of "Masse Chimique," which has been extended and improved by Guldberg and Waage, but the "Statique Chimique" is chiefly remembered for the famous controversy to which it gave rise between its author and Proust.

Berthollet considered that affinity is a force akin to gravity, and that chemical combination depends upon mechanical laws, so that an alteration in the physical conditions under which two or more substances react produces an alteration in the composition of the substances formed, and hence he concluded that elements are capable of combining in all proportions. He supported his view by experiments, but he was not careful to purify his products before analysing them, and therefore his results were erroneous. Proust, on the other hand, purified his substances by every method then known, and Berthollet was at last forced to admit constant proportions in the composition of many compounds. New investigators furnished fresh facts in support of Proust's theory of constant proportions, and the controversy ended in 1809 with the complete refutation of Berthollet's views.

JOHN DALTON

1766-1844

JOHN DALTON was born at Eaglesfield, in Cumberland, September 5th, 1766. His forefathers had lived in this village for many generations, on a small copy-hold estate, and had been Quakers from the time of John's grandfather.

John appears to have been a very precocious boy. By the time he was eleven years old he had mastered the "three R's" (reading, 'riting, 'rithmetic), and had also "gone through a course of mensuration, surveying, navigation, etc.," and when he was twelve he opened a school! At the age of fifteen he went to Kendal, where he remained eleven or twelve years, first as assistant master to his cousin, and afterwards as joint principal, with his brother, of a boarding school for boys; but John was not a successful teacher.

During these years Dalton improved his knowledge of Latin, Greek and French, and also studied Mathematics and Natural Philosophy. He was considerably helped in these studies by a Mr. Gough, a blind man, who lived at Kendal, and it was at his instigation that Dalton began his "Observations on the Weather, etc," on March 24th, 1787. He continued these observations to the end of his life, and they materially helped towards his atomic theory.

In 1793 Dalton became tutor of mathematics and natural philosophy in a Dissenting College in Manchester. He held this post for six years, and continued to live in Manchester after his resignation.

In 1804 Dalton gave a course of lectures in London on heat, mixed gases, etc., which attracted a great deal of attention. In 1822 he visited Paris and became acquainted with Laplace, Gay-Lussac, and many other eminent scientific men of the day. In the same year (1822) Dalton became a Fellow of the Royal Society, and in 1830 was elected Foreign Associate of the French Academy. He was also one of the original members of the British Association for the Advancement of Science. In 1833

Government granted him a pension of £150 a year, which three years afterwards was increased to £300 a year. He became paralysed in 1837, but partially recovered; he was taken worse in 1844, and died on July 16th, in that year. He never married.

He was very quiet and hard-working, but used to take a half-holiday once a week to play his favourite game—bowls. He would then throw off his usual sedate manner, and become as excited as a school-boy, and would chase after the ball and wave his hand in the direction he wished it to take, just like a child.

Dalton suffered from a species of colour-blindness, which has been named after him. This affection had sometimes amusing results. On one occasion he brought his mother, a sedate Quaker woman, a present of a pair of drab stockings, which everyone else pronounced to be bright scarlet, and on another he wandered about the streets of Oxford in the scarlet gown of his D.C.L. degree, thinking it to be dark green.

The great work of Dalton's life was the formulation of the atomic theory. The idea that matter is composed of small, invisible, moving particles is a very ancient one, and was taught by the Greek philosopher, Democritus (about 400 B.C.) and by Epicurus (340-270 B.C.).

Newton pictured an atom as a "solid, massy, hard, impenetrable, moveable particle," and this idea of the atomistic composition of matter was very generally held by chemists in the eighteenth and the beginning of the nineteenth centuries, but John Dalton was the first to attempt to determine the relative weights of the atoms; in fact up to his time all atoms were assumed to be of the same weight. Dalton speaks of simple and compound atoms. For instance an atom of water (a compound) consists of an atom of oxygen and of hydrogen.

Dalton first mentions atomic weights in 1803, in a paper on the absorption of gases by water and other liquids. He says: "All gases that enter into water and other liquids, by means of pressure, and are wholly disengaged again by the removal of that pressure, are mechanically mixed with the liquid and not chemically combined with it." He then goes on to enquire why water does not dissolve the same volume of every gas. He says, "This question I have duly considered, and though I am not yet able to satisfy myself completely, I am nearly persuaded that the circumstance depends upon the weight and number of the ultimate particles of the several gases, those whose particles are lightest and single being least absorbable, and the others more, according as they increase in weight and complexity. An inquiry into the relative weights of the ultimate particles of bodies is a subject, as far as I know, entirely new. I have lately been prosecuting this inquiry with remarkable success. The principle cannot be entered upon in this paper, but I shall just subjoin the results, as far as they appear to be ascertained by my experiments."

The following are some of the numbers given in his

"Table of the relative weights of the
ultimate particles of gaseous and other bodies."

Hydrogen, 1
Carbon, 4.3
Azote (Nitrogen), 4.2
Oxygen, 5.5

Water, 6.5
Sulphur, 14.4
Sulphuretted hydrogen, 15.4

In 1807 Dr. Thomas Thompson, in the third edition of his "System of Chemistry," gave an account of Dalton's atomic theory and the Law of Multiple Proportions, and the following year Dalton himself brought out a book called "A New System of Chemical Philosophy," in which he expounded his views.

The Law of Multiple Proportions is as follows: "When two elements unite in several proportions, the masses of the second element which combine with a definite mass of the first, bear a simple rational ratio to each other." Dalton discovered this law though he did not state it in the above general form. He quoted ethylene and marsh gas in support of the above law. He analysed these compounds and found that in ethylene the proportion of carbon to hydrogen is 5.4 to 1, and in marsh gas 5.4 to 2. (These figures are not quite accurate; modern investigators give 6 to 1 and 6 to 2). Dalton also pointed out that the "elements of oxygen may combine with a certain portion of nitrous gas, or with twice that portion, but with no intermediate quantity." "Nitrous gas" is our nitric oxide. The modern equations would be as follows:

$$2NO + O_2 = 2NO_2$$
$$4\,NO + O_2 = 2N_2O_3$$

Dalton supported his Law by theoretical

arguments as well as by experimental data. If the various elements consist of atoms of definite weight, and if compounds are formed by the union of these atoms, then the ratios in which the atoms combine will be expressed by whole numbers, since it is assumed that an atom cannot be divided.

Dalton gave rules in his "New System of Chemical Philosophy" for finding atomic weights. He says: "The following general rules may be adopted as guides in all our investigations respecting chemical synthesis.

1st. When only one combination of two bodies can be obtained, it must be presumed to be a binary one, unless some cause appear to the contrary.

2nd. When two combinations are observed, they must be presumed to be a binary and a ternary," &c.

By "binary," "ternary," &c., he meant consisting of two atoms, three atoms, etc. These "rules" are quite arbitrary. There is not the slightest reason why, if only one compound of any two elements is known, it should be a binary one, and Dalton himself did not always adhere to his own precepts. For example: he considered sulphuretted hydrogen a quaternary compound, consisting of one atom of sulphur and three atoms of hydrogen, though binary and ternary were unknown. He took hydrogen, with atomic weight 1, for his standard element. All that can be found from analysis of a compound is the ratio of the weights of the substances composing it. For instance, in water the ratio of hydrogen to oxygen is 1 to 8, or 2 to 16, or 3 to 24. . . . The atomic weight of oxygen is 8, 16, 24 . . . according as one atom of oxygen is combined with 1, 2, or 3 atoms of hydrogen.

Dalton did not know how to decide this point with certainty, so he formulated his rules, though he also pointed out that any atomic weight found by them ought to be checked by examining as many compounds as possible containing the given element.

Dr. Dalton made a great many atomic weight determinations, but he was not a careful experimenter, and his results are of little value; but the importance of his atomic theory cannot be over-estimated, indeed the whole fabric of modern chemistry is built upon it.

It may be mentioned that Dalton was the

first to use graphic formulae, of which the following are examples:

Oxygen	○	Hydrogen	⊙
Nitrogen	⦶	Carbon	●
Marsh gas	⊙●⊙	Olefiant gas	⊙●
Water	⊙○		

SIR HUMPHRY DAVY

1778-1829

HUMPHRY DAVY was born at Penzance in Cornwall, on December 17th, 1778. His father was a carver in wood and owned a small estate which had belonged to the family for several generations.

Humphry was very popular with his schoolfellows as he could manufacture successful fireworks, write poetical valentines, and tell capital stories. It is said when he was only eight years old he used to climb into an empty cart and tell wonderful tales to groups of delighted youngsters gathered round it.

He remained at school till he was fifteen, and two years afterwards was apprenticed to Mr. Borlase, a surgeon and apothecary in Penzance. In 1798 Mr. Gregory Watt came to lodge with Humphry's mother, and the boy would often have long talks with him on scientific subjects.

While with Mr. Borlase, Davy made numerous experiments on heat, which brought him into correspondence with Dr. Beddoes, who was so impressed with the young man's abilities that he engaged him as Superintendent of the Pneumatic Institution at Bristol. This Institution was founded by Dr. Beddoes, and was supported by subscription. It existed for the purpose of research work on gases, with the view of applying them as remedies for diseases.

In 1801 Davy was appointed Assistant Lecturer on Chemistry at the Royal Institution, and a year later he was made Professor. He gave his first lecture at the Royal Institution on the 25th of April, 1801, and at once became famous. He was a very eloquent speaker, and men of rank and women of fashion flocked to his lectures, as well as regular students. He resigned his Professorship in 1812, and was knighted April 8th of that year. Three days afterwards he married Mrs. Apreece, a widow. He spent the next two or three years in travelling with his wife.

He invented the miner's safety lamp in 1815, and in 1818 was made a baronet in recognition of this valuable invention. In 1820 he became

President of the Royal Society, and was re-elected to this office for seven years, when he resigned owing to ill-health. In 1826 he had an attack of paralysis, but recovered to some extent and was able to travel again. While at Rome in 1828 he had another attack, but again recovered sufficiently to start for home, but he never saw his native land again, and died at Geneva, May 28th, 1829.

Of Davy's many and important discoveries in the different regions of chemistry, perhaps the one that most profoundly impressed chemists of his own day, was his brilliant electro-chemical researches culminating in the isolation of potassium and sodium, and later on of the alkaline earth metals, though he did not obtain the latter in any quantity or very pure.

He began his electro-chemical work in 1800. In was known that water can be resolved into its constituents by the electric current, and it had been noticed that during the decomposition an acid appeared at the postive and an alkali at the negative pole. The acid was supposed to be nitrous or muriatic acid, and the alkali, ammonia. It had been suggested that the water itself had been converted into acid and alkali by the action of the current, and it was to decide this point that Davy began his experiments.

This investigation is worth considering in detail as illustrative of the thoroughness and skill displayed by this chemist.

He first passed the current through distilled water contained in glass vessels connected by cotton-fibre, and found nitric and hydrochloric acids near the positive pole, and soda near the negative pole. He then varied the conditions of the experiment one by one, to find out if any change was thereby produced in the products of electrolysis. He found the quantity of hydrochloric acid formed grew less and less when he used the same piece of cotton-fibre for a series of experiments, and washed it in dilute nitric acid each time before using; hence he concluded the presence of this acid was due to the connecting substance. He thought the soda might come from the glass, and tried placing the water in agate and then gold cups; a minute quantity of alkali was still formed. He then evaporated the distilled water to dryness in a silver dish and obtained a slight alkaline residue. He next redistilled the water in a silver retort before electrolysing, and this time no alkali was formed, but nitric acid still appeared near the positive pole. He thought this might be due to the presence of free nitrogen dissolved in the water from the atmosphere, so he caused his electrolysis to take place in an atmosphere of hydrogen, and found that nitric acid was no longer produced, so he concluded that "water, chemically pure, is decomposed by electricity into gaseous matter alone, into oxygen and hydrogen."

Although the above statement is of great interest, a discovery of far more importance was to follow from this water investigation, for in the course of it Davy's attention was directed to the effect of the electric current on glass, which led him to experiment with other substances, and finally with the alkalies, as he thought such a powerful agent would probably decompose them, if they were capable of decomposition.

Davy first tried the effect of the current on strong aqueous solutions of potash and soda, but he only obtained oxygen and hydrogen. He next used fused potash, and obtained small metallic globules which inflamed in the air.

Spurred on by this success, he renewed his efforts, and at his next attempt used two platinum electrodes. Davy describes his experiments as follows:

"A small piece of pure potash which had been exposed for a few seconds to the atmosphere, so as to give conducting power to the surface, was placed upon an insulated disc of platina, connected with the negative side of the battery of the power of 250 of 6 and 4, in a state of intense activity; and a platina wire, communicating with the positive side, was brought in contact with the upper surface of the alkali. The whole apparatus was in the open atmosphere.

"Under these circumstances a vivid action was soon observed to take place. The potash began to fuse at both its points of electrization. There was a violent effervescence at the upper surface; at the lower, or negative surface, there was no liberation of elastic fluid, but small globules having a high metallic lustre, and being precisely similar in visible character to quicksilver, appeared, some of which burnt with explosion and bright flame as soon as they were formed, and others remained, and were merely tarnished, and finally covered by a white film which formed on their surfaces. These globules, numerous experiments soon showed to be the substance I was in search of, and a peculiar inflammable principle the basis of potash. I found that the platina was in no way connected with the result, except as the medium for exhibiting the electrical powers of decomposition, and a substance of the same kind was produced when pieces of copper, silver, gold, plumbago, or even charcoal were employed for completing the circuit.

"The phenomenon was independent of the presence of air. I found that it took place when the alkali was in the vacuum of an exhausted receiver."

One of Davy's biographers tells us, "he (Davy) could not contain his joy, he actually bounded about the room in ecstatic delight, and some little time was required for him to compose himself sufficiently to continue the experiment."

Davy called this metal potassium, and he obtained sodium by a similar process in the same year, 1807, and afterwards he obtained calcium, barium, strontium and magnesium, but not very pure or in large quantities.

Lavoisier said that all acids contain oxygen, and the statements of this great chemist carried such weight that few thought of disputing them, and Berthollet was almost the only one to raise his voice in protest. He said since hydrocyanic acid and sulphuretted hydrogen have acid properties and yet contain no oxygen, this element is not a necessary constituent of all acids, but his view was disregarded, and even Berthollet himself assumed the existence of oxygen in muriatic acid (hydrochloric acid), though its presence had never been detected.

Scheele discovered the gas we now call chlorine in 1774. He prepared it by the action of muriatic acid on manganese ore, and called it "dephlogisticated marine acid gas." In 1785 Berthollet found that water impregnated with this gas and exposed to sunlight became converted into marine acid with evolution of oxygen, so he concluded that Scheele's gas was a compound of muriatic acid with oxygen, and this view was generally accepted. In 1808 Davy obtained potassium chloride and hydrogen by decomposing muriatic acid with potassium, and in 1809 Gay-Lussac and Thenard found that water and silver chloride are produced by the action of the above acid on silver oxide. They also effected the synthesis of muriatic acid by exposing a mixture of chlorine and hydrogen to sunlight. From these experiments they concluded that muriatic acid is either a compound of an unknown radical "muriaticum" with water and oxygen, and chlorine a compound of anhydrous muriatic acid and oxygen, *or* chlorine (oxygenated muriatic acid) is an element, and muriatic acid a compound of chlorine and hydrogen, but they considered the first hypothesis the most likely one.

Davy worked at oxidised muriatic acid and muriatic acid in 1810 and 1811, and came to the conclusion that the former is an elementary substance. He pointed out that this view agrees with Scheele's original conception of the gas expressed by the name —dephlogisticated marine acid. Chlorine, like the element oxygen, is electro positive, and like oxygen it combines directly with many metals with evolution of light and heat, e.g., copper, antimony, phosphorus, etc. He showed that oxidised muriatic acid is converted into muriatic acid by the addition of hydrogen, and not by the removal of oxygen, and he also pointed out that no oxygen can be detected in muriatic acid. He compared the actions of oxidised muriatic acid and muriatic acid on certain oxides of the metals, and showed that with a given oxide the same salt is formed by the action of either of these substances, but with the first "acid" oxygen is evolved, and with the second one water is formed. From these results he considered oxidised muriatic acid an elementary substance, and called it chlorine, from a Greek word meaning greenish-yellow. He established the elementary nature of iodine soon after its discovery by Courtois of Paris in 1812. In addition to chlorine itself Davy studied nitrogen chloride and the oxides of chlorine. Chlorine peroxide was first prepared by him in 1815, by the action of strong sulphuric acid on potassium chlorate.

It will be remembered that Davy went to Bristol in 1798 to study gases for use in medicine.

It was supposed that nitrous oxide, discovered by Priestley, had an injurious effect on animals, so Davy made a special study of this gas. He confined a little of it in a silk bag and experimented on himself by breathing it. He felt a "sensation analogous to gentle pressure on all the muscles . . . the objects around me became dazzling and my hearing more acute . . . at last an irresistible propensity to action was indulged in. . . . I recollect but indistinctly what followed; I know that my movements were various and violent." The gas received the name of "laughing gas" because many persons began to laugh after breathing it, and Davy used often to be asked to take his silk bag of gas with him to evening parties to entertain the guests. It is largely used in dentistry to produce temporary unconsciousness.

It has already been mentioned what an inestimable boon Davy's safety lamp has been to miners. Its construction depends upon two facts noticed by its inventor.

(1) The temperature at which fire damp ignites is rather high.

(2) Fire damp generates a comparatively small amount of heat when burning.

The safety lamp consists of an ordinary oil lamp with a wire gauze top and chimney. Wire gauze is such a good conductor of heat that the flame from the burning wick inside the lamp does not make the gauze hot enough to ignite fire damp outside the lamp. This gas of course can penetrate the wire gauze and will burn with slight explosion, inside the lamp, when it comes in contact with the flame, but owing to (1) and (2) it will not cause ignition of the gas outside the lamp.

JOSEPH LOUIS GAY-LUSSAC
1778-1850

JOSEPH LOUIS GAY-LUSSAC was born at St. Leonard (Haute-Vienne) December 6th, 1778. He went to Paris when he was sixteen years of age and three years afterwards entered the Ecole Polytechnique, and in 1809 he was appointed Professor of Chemistry there. In 1832 he was given the chair of general chemistry at the Jardin des Plantes. He died at Paris, May 9th, 1850. He was raised to the peerage in 1839, in recognition of the services he had rendered to Science.

Lavoisier, Fourcroy and others had endeavoured to find the volumes in which hydrogen and oxygen combine to form water; the numbers given were 23 volumes of hydrogen to 12 volumes of oxygen, and 205.2 vols. of hydrogen to a 100 vols. of oxygen; but in 1805 Humboldt and Gay-Lussac made a fresh determination, and they found that 2 vols. of hydrogen combine with 1 vol. of oxygen to form water, and that this volume relation is unaffected by temperature. Gay-Lussac discovered that the volume of a given mass of any gas varies directly as the absolute temperature of the gas, if the pressure upon it remains constant, and he knew Boyle's law, viz: that the volume of a given mass of any gas varies inversely as the pressure upon it if the temperature of the gas remains constant, so when Gay-Lussac again turned his attention to the volumes of gases, three years after his water investigation, he was able to calculate his results for a single pressure and temperature, from his observations at various pressures and temperatures.

He found that two volumes of carbon-dioxide are formed by the union of two volumes of carbon monoxide with one volume of oxygen; that is, the volume of the compound formed : sum of volumes of its constituents : : 2 : 3.

Two volumes of nitrogen and one volume of oxygen form two volumes of nitrous oxide; here again contraction takes place, and the volume of the compound formed : sum of volumes of its constituents : ; 2 : 3.

One volume of nitrogen unites with one volume of oxygen to form two volumes of nitric oxide; no contraction takes place here, and the volume of the product is equal to the sum of the volumes of its constituents.

One volume of nitrogen condenses with three volumes of hydrogen to form two volumes of ammonia; here the volume of the product is half the volume of its constituents.

From these facts Gay-Lussac concluded that gases combine chemically in simple proportion by volume, and that the volumes of gaseous products always bear a simple relation to the volumes of the combining gases. The above statement is known as Gay-Lussac's Law of Volumes, and was announced in 1809.

In 1808 Gay-Lussac and Thenard obtained potassium in larger quantities than Davy, by passing melted potash over iron turnings raised to a white heat. The iron took up the oxygen, and potassium and hydrogen were liberated. The potassium was condensed in a copper vessel containing naptha. These two chemists also obtained boron by the action of potassium on boric acid, and discovered potassamide.

Iodine was discovered in 1812, and Gay-Lussac examined it and pointed out its analogy with chlorine; he also discovered hydriodic acid.

In 1811 Gay-Lussac and Thenard devised a method of analysing organic compounds. The organic substance was burnt with potassium chlorate, which supplied the oxygen necessary for combustion, and the mixed gases evolved were collected and measured. The carbon-dioxide was then absorbed, and the residual volume of oxygen measured.

The quantity of water formed was calculated from Lavoisier's equation,

Substance + oxygen employed = carbonic anhydride + water

and so the carbon, hydrogen and oxygen present in the original substance were all determined. The above chemists used this method to find the composition of sugar, gum, oxalic, tartaric and citric acids, and many other substances, but the method does not give very accurate results. Gay-Lussac also discovered cyanogen, and the method for determining vapour densities which bears his name.

JOHANN JACOB BERZELIUS

1779-1848

JOHANN JACOB BERZELIUS was the son of a schoolmaster, and was born August, 1779, at Wäfersunda, a village in East Gothland, Sweden.

Berzelius was left an orphan when he was nine years old, and was brought up by his grandfather. He went to school at Linköping, and subsequently entered the University of Upsala as a medical student. He obtained his M.B. degree in 1801, and a few years later went to the medical school at Stockholm as Professor of Chemistry. He remained at Stockholm for nearly fifty years, and his laboratory there became famous throughout Europe. Many distinguished chemists studied there, including Wöhler and Mitscherlich.

Berzelius was elected President of the Stockholm Academy of Sciences when he was thirty-one, and a few years afterwards he became a Foreign Fellow of the Royal Society, and was awarded the Copley Medal in 1836. He was made a baron by the King of Sweden in recognition of his scientific work.

The laboratory of this famous chemist was extremely simple. Wöhler tells us when he entered as a student there was no gas, draught cupboards or ovens, only two plain tables and a little simple apparatus, while the furnace and sand-baths were situated in the adjoining kitchen used for ordinary household purposes. In this poorly equipped room Berzelius made his brilliant discoveries and researches of far-reaching importance.

The idea of atomic weights originated with Dalton, and he was the first chemist who attempted to find them. His indication of the reasoning to be followed in making these determinations was of great value to subsequent investigators, though his numerical results were of little use. Berzelius was the first chemist to accurately determine atomic weights. He found values for most of the elements known in his day, and the fact that many of his numbers agree closely with those given by much later workers testifies to the skill and care he brought to bear on his experiments. He calculated all his results with reference to Oxygen = 100. Expressed in terms of Oxygen = 16 some of his best values are as follows:

Berzelius' Value	Modern Value
Calcium, 41.03	40.1
Chlorine, 35.47	35.45
Arsenic, 75.33	75.0

Before the atomic weight of an element can be decided two things are necessary.

1. As many compounds as possible containing the element must be analysed to find its "equivalent weight" or the proportion by weight in which it combines with the element chosen as the standard, or with some other element whose atomic weight is known.

2. It must be known how many atoms of the element under consideration are present in one of the compounds analysed.

In water, for instance, the proportion of hydrogen to oxygen is 1 to 8, or 2 to 16, or 3 to 24, etc. If hydrogen be taken as the standard element with assumed atomic weight 1, the atomic weight of oxygen is 8, 16, 24—according to the number of atoms of oxygen combined with one atom of hydrogen. Which of these numbers is the correct one cannot be decided by a purely quantitative analysis.

Dalton realised this and formulated his "rules." Berzelius realised this also, and condensed and extended Dalton's rules as follows:

"One atom of one element combines with 1, 2, 3, or more atoms of another element."

"Two atoms of one element combine with 3 or 5 atoms of another element."

The above rules are just as arbitrary as Dalton's, but Berzelius unlike Dalton did not mistrust all information he had not acquired himself, and to fix upon the correct atomic weight he availed himself (though only for elementary gases) of Gay-Lussac's generalisation. "Equal volumes of gases contain equal numbers of atoms." Mitscherlich's Law of Isomorphism discovered, 1818, "Compounds, the atoms of which contain equal numbers of elementary atoms similarly arranged, have the same crystalline form;" and Dulong and Petit's Laws discovered, 1819, "The atoms of all solid elements have the same capacity for heat," or in other words, "The product of the specific heat and the atomic weight is constant."

Berzelius applied Gay-Lussac's generalisation regarding volumes to determine the number of atoms of each element present in water. Since (he argued) equal volumes of oxygen and hydrogen contain the same number of atoms, and 2 volumes of hydrogen unite with 1 volume of oxygen to form water, therefore 2 atoms of hydrogen unite with 1 atom of oxygen to form water; atom and volume, in the case of elementary gases, being interchangeable terms.

As mentioned above, Berzelius only accepted Gay-Lussac's generalisation for simple gases; there was a difficulty in applying it to compound ones.

In Dalton's book "A New System of Chemical Philosophy," the author says he once thought that equal volumes of all gases contain the same number of particles, but he abandoned this view as contrary to known facts. He says, "One atom of nitric·oxide consists of one atom of nitrogen and one of oxygen. If now, there were the same number of atoms in equal volumes, one volume of nitric oxide should be formed by the combination of one volume of nitrogen with one of oxygen, but according to Henry's experiments, about two volumes are produced ; hence nitric oxide could only contain half as many atoms in the same space as nitrogen or oxygen," so he rejected Gay-Lussac's conclusion that "equal volumes of gases contain equal numbers of atoms."

Avogadro was the first to show how Gay-Lussac's Law could be brought into harmony with the atomic theory.

It will be remembered that Dalton spoke of simple atoms and compound atoms. Oxygen consists of simple atoms, water of compound ones. Avogadro said all substances, elements and compounds consist of compound atoms or molécules intégrantes (now called molecules), and all molecules whether of compounds or elements, consist of two or more molécules élémentaires, or atoms, but the atoms that build up a molecule of a simple substance or element are all exactly alike, while the atoms that up build a molecule of a compound substance are different. Avogadro now stated "Equal volumes of all gases, at the same temperature and pressure, whether elementary or compound, contain the same number of molecules," and he quotes nitric oxide in support of his hypothesis.

Two volumes of nitric oxide consist of one volume of nitrogen and one volume of oxygen; that is, two gases have united to form a new gas without any change of volume. How can this have taken place? Only by supposing that every molecule of nitrogen and oxygen consists of two atoms, and that a molecule of nitric oxide also consists of two atoms, one atom of nitrogen and one atom of oxygen. Avogadro also pointed out that from his hypothesis the molecular weight of gaseous elements are proportional to their densities, a principle that has been used again and again in molecular weight determination.

But, as is so often the case, Avogadro's reasoning and theories were disregarded in his own day, and it was not until many years after they were first published that Avogadro's views were accepted as correct.

To return to the Swedish chemist. Berzelius' dualistic system, or electro-chemical hypothesis, ranks amongst the most important of this brilliant chemist's work. Ladenburg says, "He made it his life's task to establish in chemistry a uniform system which should be applicable to all the known facts; and he accomplished it"; and again: "The chemical edifice which Berzelius erected was a wonderful one, as it stood completed (for inorganic substances) at the end of the third decade of the nineteenth century. Even if it cannot be said that the fundamental ideas of the system proceeded exclusively from himself, and if he was indebted to Lavoisier, Dalton, Davy and Gay-Lussac for a great deal, still it was he who moulded these ideas and theories into a connected whole, adding also much that was original."

According to Berzelius every atom has two poles at which electricity is accumulated, positive electricity at the positive pole, and negative electricity at the negative pole. Notwithstanding the presence of both kinds of electricity the whole atom is unipolar, since the strength of one pole is always greater than the other.

When two simple atoms unite to form a compound one, the positive electricity in one atom neutralises the negative electricity in the other one, and the action is accompanied by heat and light. The compound atom is still positive or negative, since only one pole of each of the reacting atoms is neutralised at combination.

Berzelius considered affinity to be due to different electrical states. Since opposite electricities attract, combination takes place most readily between a strongly negative and a strongly positive atom, but combination can take place between two similarly electrified atoms, because in a $\left\{\begin{matrix}\text{positive}\\ \text{negative}\end{matrix}\right\}$ atom there is some $\left\{\begin{matrix}\text{negative}\\ \text{positive}\end{matrix}\right\}$ electricity that can be discharged by the $\left\{\begin{matrix}\text{positive}\\ \text{negative}\end{matrix}\right\}$ electricity of the other atom. Chemical combinations are affected by temperature because variations of temperature produce corresponding changes in intensity of polarity, or the quantity of electricity at the poles.

Since a compound atom formed by the union of two simple atoms (compound atom of the first order) has a preponderance of positive or negative electricity, it is capable of entering into combination with a simple atom to form a compound atom of the second order, or with a compound atom of the second order to form a compound atom of the third order. Thus Berzelius considered every compound atom (or molecule as we should now say), however complex, to be a dual structure and to consist of two parts, one part negatively, the other part positively electrified.

He explained electrolysis by assuming that the action of the electric current restores the original polarity to each part of the dual structure, thus causing decomposition.

Lavoisier taught that all acids contain oxygen. It has been mentioned that Berthollet showed that hydrocyanic acid and sulphuretted hydrogen contain no oxygen, and yet have acid properties. The idea of oxygen as the acidifying principle is incompatible with Berzelius' electro-chemical theory, as according to it a base is an electro-positive oxide, and an acid an electro negative oxide that is oxygen is a constituent of both bases and acids, and therefore cannot be an acidifying principle ; so Lavoisier's theory was rejected by many chemists.

At first Berzelius applied his dualistic theory to inorganic substances only, but afterwards he extended it to embrace organic substances as well.

Lavoisier, Berthollet and Fourcroy introduced a system of chemical nomenclature. Berzelius perfected this system and introduced a method of notation which is almost identical with the one in present use. The practice of representing an atom of an element by the initial letter of its Latin name originated with him.

Berzelius improved Gay-Lussac's method of organic analysis. He originated the terms *isomeric*, *metameric*, and *allotrophy*, and discovered and investigated the sulpho salts. He discovered selenium in 1817. This element is found principally in certain iron pyrites, and when this ore is roasted for the preparation of sulphuric acid, a red deposit containing selenium settles in the chambers, and it was here Berzelius found it. He also found thorium in 1828 in a mineral from the island of Lövön in Norway.

Berzelius was the first to obtain impure silicon in 1810, by fusing together carbon and silica. In 1823 he heated potassium silicofluoride with metallic potassium, and obtained silicon as a brown amorphous powder after repeatedly treating the ignited residue with water. In 1815 Berzelius proved silica to be an acid anhydride.

MICHAEL FARADAY

1791-1867

MICHAEL FARADAY was born at Newington in Surrey, on the 22nd September, 1791. Soon afterwards the family moved to London, but owing to the ill-health of Michael's father, a blacksmith, the Faradays were always very poor; nevertheless they managed to send Michael to a day school, where he learnt reading, writing and arithmetic. At the age of twelve he went as errand-boy to a bookseller, and when he had been in his situation a year, his master took him as apprentice without a premium, in consideration of his previous faithful service.

Through the instrumentality of Mr. Dance, one of his master's customers, Michael was enabled to hear Sir Humphry Davy lecture at the Royal Institution. Faraday took notes of the lectures and afterwards wrote them out fully, illustrated them with drawings, and sent them to Sir H. Davy with a note, telling of the writer's wish to escape from trade and enter on a scientific career, and some time afterwards Sir Humphry took him as his Laboratory Assistant. In the autumn of 1813 he went abroad with his master in the capacity of amanuensis, and travelled through France, Italy and Switzerland. They both returned to England in 1815, and the young man resumed his duties at the Royal Institution.

Faraday delivered his first lecture January, 1816, at the City Philosophical Society on "The General Properties of Matter." He spared no pains in the preparation of his lectures, and even took lessons in elocution that he might deliver them in a pleasing manner. Eleven years afterwards, in 1827, he began to lecture at the Royal Institution, and for thirty-eight years his lectures there were a source of delight to his varied audiences.

In 1821 Faraday married. In 1829 he was made a member of the Scientific Advising Committee of the Admiralty, and in 1836 he was appointed Scientific adviser to the Trinity House. The Government gave him a pension in 1835 in recognition of his services, and in

1858 the Queen granted him a house on Hampton Court Green, where he lived till his death on August 25th, 1867.

He received ninety-five honorary titles from various Scientific Societies in Europe and America, including that of Fellow of the Royal Society in 1824.

He was one of the greatest experimentalists in physical science that England has ever had, and his winning and upright character, and deep personal piety, command admiration no less than his magnificent intellectual gifts.

Monge and Cluet condensed sulphur dioxide about 1800, and Northmore condensed chlorine in 1806, but Faraday was the first chemist to systematically apply himself to the liquefaction of gases, and it was not until he had published his first results that he became aware of the earlier work of the above named chemists.

In 1823 Faraday liquefied chlorine. Acting on a suggestion of Sir Humphry Davy he sealed up some crystals of chlorine hydrate in a bent tube, and heated one limb of the tube and cooled the other; an oily liquid collected in the cool limb, which Faraday concluded could only be liquid chlorine. Afterwards he liquefied carbon dioxide, hydrochloric acid, sulphur dioxide, cyanogen and ammonia by a similar method. He introduced some substance that would readily yield up the gas required into one of the limbs of a bent tube, and then sealed up the other end. He warmed the end containing the substance and the gas distilled over into the other end of the tube, where it condensed to a liquid under the pressure exerted by the gas itself. Since by Boyle's Law, "The volume of a given mass of gas varies inversely as the pressure, the temperature remaining constant," considerable pressures were produced in this way by using comparatively small tubes.

Faraday's experiments were conducted on a small scale, but Thilorier (1835) liquefied carbon dioxide on a large scale, and showed that a temperature of —100° could be obtained by mixing liquid or solid carbon dioxide with ether.

Faraday in 1845, by means of this cooling mixture, obtained hydrogen iodide, hydrogen bromide, sulphur dioxide, hydrogen sulphide, nitrous oxide, cyanogen and ammonia in the solid state, but hydrogen arsenide, ethylene, silicon fluoride, boron fluoride and chlorine in the liquid state only.

Benzene was discovered by Faraday in 1825 in some vessels of Oil Gas belonging to the Portable Gas Company.

The most important of Faraday's work was in connection with electricity, and belongs more to the region of physics than chemistry. However, since many of his discoveries have been of immense importance to chemistry, they must be noticed here.

His attention was first turned to the consideration of electrical phenomenon by Œrsted's discovery of the effect of a current upon a magnet, and in 1831 Faraday discovered magneto-electric induction, and in 1833 the Law that bears his name.

"When equal quantities of electricity pass through different electrolytes, equivalent quantities of these electrolytes are decomposed."

Conductors, or bodies which allow electricity to pass through them, may be divided into two classes:

1. Conductors which are not decomposed when the current passes through them, e.g., metals and carbon.

2. Conductors which suffer decomposition during the passage of the current, e.g., salts, acids, bases.

The members of this 2nd class of conductors are called electrolytes. Faraday introduced the term *ion* to designate the two constituent parts into which an electrolyte can separate. The cations carry the positive electricity and travel towards the negative pole or cathode, while the anions carry the negative electricity and travel towards the positive pole or anode. The cations are hydrogen and the metals; the anions are the hydroxyl group O H, acid radicles, halogens.

The "equivalent" of an *ion* is its weight divided by its valency. For example, the equivalent of chlorine is $\frac{35.5}{1} = 35.5$.

The equivalent of SO_4 (a divalent group) is

$$\frac{32 + 16 \times 4}{2} = 48$$

Between the years 1836 and 1838 he did important work on frictional electricity, and discovered the specific inductive capacity in insulators or dielectrics, which has been of great use in submarine telegraphy. Faraday also found (1846) that some substances which are not optically active under ordinary circumstances acquire the power of rotating the plane of polarised light when brought into a magnetic field, or placed within a coil of wire conducting an electric current.

JEAN BAPTISTE ANDRE DUMAS

1800-1884

JEAN BAPTISTE ANDRE DUMAS was born on 14th July, 1800, at Alais in the south of France, where his father was town-clerk. Jean attended a school in his native town till he was fourteen years old, when he was apprenticed to an apothecary in Alais. However, he left Alais when he was sixteen, and went to Geneva, where he entered the pharmaceutical laboratory of Le Royer.

When he was twenty-two years old Baron Humbolt called upon him and asked the young man to be his cicerone during his stay at Geneva. The Baron was a fluent talker, and so fired Dumas' imagination with stories of Gay-Lussac, Thénard and other celebrities, that after the traveller's departure the aspiring young chemist felt that Paris was the one place in the world for him, and to Paris he went within the year. There he soon became friendly with the foremost men of science and obtained the post of Répétiteur de Chimie at the Ecole Polytechnique, and soon afterwards that of Professor of Chemistry at the Athenaeum. In 1826 he married Mdlle. Hermine Brongniart.

The years that followed were full of important work, and in 1832 he founded and supported at his own expense a laboratory for chemical research, but owing to loss of funds he had to close it in 1848. In this year (1848) he began his political career and was elected a member of the National Assembly, and soon afterwards was appointed Minister of Agriculture and Commerce. He was made a Senator on the restoration of the Empire, and in 1855 became Vice President of the Municipal Council of Paris, President in 1859, and Master of the Mint in 1868. He retired from this office and from public life in 1870. He died at Cannes 11th April, 1884.

He received honours from most of the scientific societies of Europe. He became a Foreign Member of the Royal Society in 1840, and was awarded the Copley Medal in 1843. He also was made a Knight of the Prussian Order of Merit, and was given the Grand Cross of the Legion of Honour.

Dumas won his first laurels in the fields of botany and physiology, where he did work in conjunction with Coindet and Prévost. When he was about twenty-two years of age Biot's Treatise on Physics attracted his attention, and Dumas thought he would determine the thermal expansion of the compound ethers (now called ethereal salts, or esters) but he was unable to carry out his investigation to a satisfactory conclusion owing to the difficulty of obtaining sufficiently pure compounds for his experiments. But he became deeply interested in the ethers and returned to their study later on, and published a paper on this subject in conjunction with Boullay in 1828.

At that time alcohol was supposed to be formed by the union of one volume of water vapour with one volume of olefiant gas, and ether by the union of one volume of water vapour with two volumes of olefiant gas.

Olefiant Gas C_2H_4
Alcohol $C_2H_4{\cdot}H_2O$
Ether $(C_2H_4)_2{\cdot}H_2O$

Dumas wrote C_4H_4 and similarly for the other formulae as he took $C = 6$ instead of $C = 12$.

These chemists considered that olefiant gas played the part of a radical in a whole series of compounds, and compared it with ammonia in a corresponding series of ammonium salts

Olefiant Gas C_2H_4	NH_3 Ammonia
Hydrochloric ether $2C_2H_4 + HCI$ (modern notation, ethyl chloride C_2H_5Cl)	$NH_3 + HCl$ sal ammoniac
Nitrous ether $C_2H_4 + HNO_2$	$NH_3 + HNO_2$ Ammonium nitrite
Alcohol $C_2H_4 + H_2O$	$NH_3 + H_2O$ aqueous ammonia

Berzelius was at first opposed to this view, but afterwards accepted it for a time and named the radical C_2H_4 *etherin.*

The *etherin theory*, as it was called, was never generally accepted, partly because it only applied to a small number of compounds, and partly because the compound ethers (ethereal salts or esters) could not then be prepared by methods analogous to the ammonia compounds. Nevertheless this theory did good, since it directed attention towards the conception of radicals, and also helped to break down the barrier between organic and inorganic substances, by showing that the two classes contain comparable groups of substances.

During his investigation of the compound ethers (esters) Dumas discovered oxamide and ethyl oxamate.

When wood is heated in closed vessels out of contact with air, and the distillate condensed, it separates on standing into two layers, a brown aqueous layer, and wood tar. Boyle examined the aqueous layer (1661) and found that it concontains a volatile liquid which he called wood-spirit, and Taylor pointed out in 1812 that this liquid resembles alcohol ; Dumas and Péligot in 1834 succeeded in obtaining the wood-spirit in a pure form, and found its vapour density. They showed that it is analogous to ordinary alcohol, and forms compound ethers and an acid similar to acetic acid. They gave it the name of *methyl alcohol*, methyl being derived from two Greek words signifying *wine* and *material*. These two chemists also showed that spermaceti on saponification gives a substance whose chemical reactions resemble those of alcohol.

The discovery of these two alcohols was very important, because Gerhardt pointed out in 1843-1845 that methyl, ethyl (ordinary) and cetyl alcohol are members of a homologous series, whereupon chemists began to search for the missing members lying between ethyl and cetyl alcohol.

Berzelius determined the atomic weights of many of the elements, and his reputation was so great that his numbers were unquestioned until some organic compounds containing only carbon and hydrogen were analysed. The carbon was oxidised to carbon dioxide and the hydrogen to water, both products weighed, and the weight calculated of each element present in the original substance. But the sums of the weights of carbon and hydrogen so calculated came to *more* than the weight of the substance originally taken, so chemists were forced to the conclusion that Berzelius had ascribed a wrong value to carbon or oxygen, or to both. A knowledge of the ratio of the atomic weights of carbon, hydrogen, and oxygen is absolutely essential to analytical chemistry as so many other elements combine with one or other of these three, so Dumas set himself the task of clearing up this point, and in 1840, in conjunction with his pupil Stas, tried to determine the ratio of carbon to oxygen in carbon dioxide.

Every conceivable precaution was taken to insure accuracy.

The oxygen used was freed from any contamination of carbon dioxide by standing over potash solution. The oxygen was then passed successively through tubes containing: (1) pumice-stone moistened with strong caustic potash solution; (2) dry solid caustic potash; (3) glass moistened with boiled sulphuric acid; (4) pumice-stone moistened with sulphuric acid.

The carbon undergoing combustion was put in a platinum boat inside a porcelain tube. During combustion this tube was heated to redness, and the gas evolved passed over red-hot copper oxide, to oxidise any carbon monoxide to carbon dioxide. The carbon dioxide was then absorbed in a series of absorption tubes. Dumas and Stas made five combustions of natural graphite, four of artificial graphite, and five of diamond, and as the mean of their results found 11·9 for the atomic weight of carbon.

In 1843 Dumas and Stas repeated the synthesis of water carried out by Berzelius and Dulong in 1820, and found as the mean of nineteen experiments that two parts by weight of hydrogen unite with 15·9608 parts by weight of oxygen to form water.

Dumas and Boussingault determined the proportions by weight in which oxygen and nitrogen are present in the air. The three researches last mentioned are classical in the annals of chemistry.

Dumas determined the atomic weights of between twenty and thirty elements—a stupendous task, and one which occupied his attention for several years. Most of his results were published in 1859.

He undertook this work partly because he mistrusted Berzelius' results owing to the error that chemist had made in the atomic weight of carbon (though it may be mentioned in passing that it was almost the only weight considerably at fault) and partly because of Prout's hypothesis. Prout, in 1815, put forward the idea that the atomic weights of all the elements might be expressed by integral multiples of the atomic weight of hydrogen. The chief interest of this idea lies in the fact that, if true, it points strongly to the assumption of a primordial form of matter. Dumas at first accepted Prout's hypothesis, but after he had made several atomic weight determinations he suggested that half the atomic weight of hydrogen should be taken as the standard, and later on he reduced this value to a quarter.

Analytical chemistry is greatly indebted to this chemist.

He devised a method for estimating nitrogen in organic compounds which is still in common use. Briefly, the method consists in intimately mixing the organic substance with cupric oxide, heating in a combustion tube and measuring the volume of nitrogen evolved. The method is fully described in all text-books on Practical Chemistry, and is one of the standard experiments performed by students taking a Laboratory Course.

Victor Meyer's Vapour Density method has to a great extent superseded that of Dumas, but the latter is still used for substances which are difficult to volatilise. In this method the liquid whose vapour density is required is introduced into a weighed globe-shaped vessel, the neck of which is drawn out into a fine point. The bulb is heated in an oil bath until all the liquid is converted into vapour, the end is then sealed up and the bulb weighed when cold.

The first weighing gives the weight of the globe full of air, and the second weighing gives the weight of the globe full of vapour, and from these results the vapour density at normal temperature and pressure can be calculated.

Dumas discovered the true nature of silica. He pointed out that the fatty acids form a homologous series, of which seventeen members were then known and nine were missing. He discovered anthracene and established the composition of chloroform.

The Substitution Theory of Dumas, elaborated by Laurent, is very important.

In 1815 Gay-Lussac found that prussic acid is converted into cyanogen chloride by treating with chlorine, the hydrogen in prussic acid being replaced by an equal volume of chlorine (prussic acid C N H, cyanogen chlorine C N Cl). He also found that when beeswax is bleached by chlorine it loses hydrogen and takes up an equal volume of chlorine. Faraday in 1821 showed that by the continued action of chlorine on Dutch liquid (ethylene dichloride $C_2H_4Cl_2$) is converted into perchloroethane (C_2Cl_6), the chlorine replacing an equal volume of hydrogen. Wöhler and Liebig in their classical research on the derivatives of benzoic acid found that chlorine converts oil of bitter almonds (benzaldehyde) into benzoyl chloride, another example of the replacement of hydrogen by chlorine. But all these facts were disregarded until 1834.

At a soirée at the Tuileries given by Charles X. in that year, the guests were greatly annoyed by acid vapours, which apparently proceeded from the wax candles. Alexandre Brongniart, who was chemical adviser to the King, requested his son-in-law, Dumas, to try to discover the reason these candles were so objectionable, and he soon found out that chlorine had been used to bleach the wax for the candles, and that the fumes were hydrochloric acid. Dumas felt sure that the chlorine must have entered into the actual composition of the candles, to be present in such quantity, and he began to investigate the action of chlorine on organic compounds.

He found that chlorine can replace an equal volume of hydrogen in oil of turpentine, and he asserted that chlorine has the power of replacing hydrogen, atom for atom, in certain substances, and proposed that this phenomenon should be called metalepsy, but this term soon dropped out of use.

Later on, Dumas formulated the following Laws of Substitution.

1. "If a body containing hydrogen is subjected to the dehydrogenating action of chlorine, bromine, iodine, oxygen, etc., for each atom of hydrogen, which it loses, it takes up one atom of chlorine, bromine or iodine, or half an atom of oxygen.

2. If the body besides hydrogen contains oxygen, the same rule holds good without modification.

3. If, however, it contains water, the latter first loses its hydrogen without replacement, and then only hydrogen is removed and replaced as stated above.

The third rule explains his view of the formation of chloral. It will be remembered Dumas wrote Alcohol $C_2\ H_4 + H_2O$.

$$\underset{\text{alcohol}}{(C_2H_4 + H_2O)} + 2\ CI = \underset{\text{aldehyde}}{C_2H_4O} + 2\ H\ Cl$$

$$C_2H_4O + 6\ Cl \quad = \quad \underset{\text{choral}}{C_2HCl_3O} + 3H\ Cl$$

Dumas included oxidations under the head of substitution. Thus in the formation of acetic acid from alcohol he supposed an atom of oxygen to replace two atoms of hydrogen in alcohol, and a further atom of oxygen to combine with the hydrogen turned out to form water.

$$\underset{\text{alcohol}}{(C_2H_4 + H_2O)} + 2\ O = \underset{\text{acetic acid}}{(C_2H_2O + H_2O)} + H_2O$$

Laurent after making a careful study of the phenomena of substitution declared that Dumas' rules were insufficient and sometimes incorrect, as substitution was not always by equivalent quantities. He also said that when chlorine and bromine did replace equivalent quantities of hydrogen, the chlorine or bromine to a certain extent played the part of the displaced hydrogen, and the new substance, formed by substitution, had similar properties to the original substance.

This drew down an attack from Berzelius, for it was in direct opposition to his electro-chemical theory that electro-negative elements, like chlorine and bromine, could replace an electro-positive element like hydrogen, without causing a change in the nature of the substance. Dumas agreed with Berzelius at first, and said his law was merely a quantitative one, and that he did not hold with Laurent's views as to unchanged properties. But after Dumas discovered trichloracetic acid he came round to Laurent's opinion.

In 1839 Dumas converted his substitution theory into his theory of types.

1. "The elements of a compound body can in many cases, be replaced by equivalents of other elements or of compound bodies, which play the part of simple ones.

2. If such a substitution takes place, equivalent for equivalent, the compound in which the replacement has occurred retains its *chemical type*, and the element or group which has been taken up, plays in it the same part as the element which has gone out."

The following are examples of types:

$$\left\{\begin{array}{l}\text{Acetic acid } C_2H_40_2 \\ \text{trichlorecetic acid } C_2HCl_30_2\end{array}\right.$$

$$\left\{\begin{array}{ll}\text{Chloroform} & C\ H\ Cl_3 \\ \text{Bromoform} & C\ H\ Br_3 \\ \text{Iodoform} & C\ H\ I_3\end{array}\right.$$

The above are *chemical types*,

Dumas also recognised *mechanical types*, which are groups of substances possessing entirely different properties but containing the same number of equivalents.

Marsh gas $C_2H_2H_6$
Formic Acid $C_2H_2 0_3$
Chloroform $C_2H_2Cl_6$

FRIEDRICH WOHLER

1800-1882

FRIEDRICH WOHLER was born at Eschersheim, 31st July, 1800. His father, August Anton Wöhler, was one of the leading citizens of Frankfort. Like Liebig, Wöhler did not distinguish himself during his school days, and instead of conning his task would spend his time experimenting on his own account and collecting specimens. His scientific tastes were encouraged by Dr. Buch, a retired physician, who helped him with chemistry and physics. The elder Wöhler taught his son sketching and made him familiar with the best German literature, and above all instilled in him that love of outdoor life and exercise to which he probably owed his exceptionally good health.

Wöhler studied medicine at the University of Marburg, and obtained his degree in 1823. He worked for a time in the Heidelburg laboratory under Gmelin, and went from there to study under Berzelius at Stockholm, where he remained for a year, and then spent two months travelling with his instructor in Southern Sweden and Norway. During these months spent in daily intercourse a warm friendship sprang up between the two, which lasted till Berzelius' death, and was not destroyed by occasional controversies on chemical theory.

In 1825 Wöhler was appointed teacher of chemistry at a newly-founded Trade School in Berlin. In 1831 he removed to Cassel, and while there lost his wife, after being married only about two years. In 1836 he was appointed Professor of Chemistry in the University of Göttingen, where he remained until his death, on 23rd September, 1882.

He received numerous honours from different scientific societies, including Foreign Membership of the Royal Society in 1854, and the award of the Copley Medal in 1872.

In 1828 Wöhler accomplished the most important work of his life—the synthesis of urea.

At that time there was a sharp division between organic and inorganic chemistry.

Although some organic compounds had been transformed into others of a kindred nature by dry distillation and by treatment with acids and alkalies, no organic substance had been wholly built up from purely inorganic materials ; indeed this was thought an impossible achievement, as all organic substances were supposed to be produced by the influence of a "Vital Force" possessed exclusively by living organisms. Professor Hofmann says of this discovery : "The synthesis of urea was an epoch-making discovery in the real sense of that word. With it was opened out a new domain of investigation, upon which the chemist instantly seized. The . . . present generation . . . is constantly gathering rich harvests from the territory won for it by Wöhler."

Wöhler found that when an aqueous solution of ammonium cyanate is warmed, or allowed to stand, it is transformed into urea. This change can be represented thus :

$$\mathrm{N} \vdots \mathrm{C.\,ONH_4} = \mathrm{NH{\cdot}_2\,CO.NH_2}$$

Ammonium cyante urea.

The most important of Wöhler's other work on organic chemistry was done in conjunction with Liebig, and is considered in the pages devoted to that chemist.

Wöhler, in 1827, was the first to prepare aluminium in a pure state. He obtained it, as a grey powder, by fusing chloride of aluminium with potassium in a closed crucible. Later on he improved this method, and passed the vapour of aluminium chloride over potassium, and succeeded in obtaining the metal in the form of globules. Many years afterwards Sainte-Claire Deville applied this method to prepare aluminium on a commercial scale, and had the first bar of aluminium produced at the works struck into medals with an image of Napoleon III. on one side and Wöhler, 1827, on the other.

Gay-Lussac prepared amorphous boron, but the crystallized variety was unknown until 1856, when Wöhler and Deville obtained it by strongly igniting boron trioxide with aluminium in a crucible surrounded with charcoal to prevent access of oxygen. During the process graphite-like laminae were formed, which they showed to be a compound of boron and aluminium $Al\,B_2$

Boron nitride was known, having been first prepared in 1842 by Balmain by heating boron trioxide with potassium cyanide, but Wöhler and Deville gave a new method of preparing this substance, namely, by heating to redness, in a platinium crucible, one part of anhydrous borax with two parts of sal-ammoniac.

These two chemists were also the first to prepare crystallized silicon (the amorphous variety was known) by throwing a mixture of three parts of potassium silico fluoride, one part of finely divided sodium, and one part of zinc into a red-hot crucible, which was then heated to fusion for some time. On cooling, a button of zinc was formed containing crystals of silicon which remained as octahedral crystals after dissolving the zinc in acids.

Wöhler and Buff discovered silicon hydride in 1857, and prepared it by passing an electric current through a solution of sodium chloride, the positive pole of the battery being an alloy of aluminium and silicon. Afterwards Wöhler and Martius obtained it by treating an alloy of magnesium and silicon with hydrochloric acid. Wöhler pointed out that the silicon hydride thus prepared contains free hydrogen. This chemist was the first to obtain metallic beryllium by fusing beryllium chloride with potassium, and he also discovered hydroquinone.

JUSTUS LIEBIG

1803-1873

Justus Liebig was born at Darmstadt, May 12th, 1803. He began to manipulate chemicals when quite a small child, for his father sold colours and would often allow his little son to help him to manufacture them. Justus was a failure as a schoolboy; he could not remember his lessons, and was once publicly reprimanded, and asked what he thought would become of him if he did not learn anything. The youth promptly replied he would be a "chemist," to the great amusement of masters and pupils, who little dreamed that some day all the scientific societies of the world would vie with each other in showing honour to this "dullard."

Liebig was apprenticed to an apothecary at Heppenheim when he was about fifteen, but the mere mixing of drugs did not satisfy his chemical aspirations, and he began experimenting on his own account in his attic. Various accidents occurred, culminating in an explosion which blew out his room window, and it is not surprising to learn that his master, dreading what might happen next, sent him home to his father.

Justus was now sixteen and eager for knowledge, and at last persuaded his father to enter him as a student at Bonn University. Here he was Kastner's favourite pupil, and when this chemist left Bonn for Erlangen, Liebig went with him, and graduated there as Doctor of Philosophy in 1822. Soon afterwards the Grand Duke of Hesse-Darmstadt granted him a small pension, which enabled the young man to study in Paris.

In 1823 be became acquainted with Alexander von Humboldt, and through his kind offices was admitted to the laboratory of Gay-Lussac.

Liebig was appointed Extraordinary Professor of Chemistry at Giessen in 1824 and Ordinary Professor in 1826. He remained there till 1852 when he went to the University of Munich as Professor of Chemistry. He continued working here up to his death, April 18th, 1873.

Most of the Scientific Societies of Europe were proud to number Liebig amongst their members. In 1845, Ludwig II., Grand Duke of Hessen, bestowed on him the title of baron, and a monument erected to perpetuate his memory was unveiled at Darmstadt, May 12th, 1877.

Inorganic analysis, both qualitative and quantitative, was fairly advanced by the beginning of the nineteenth century, but organic analysis was still in its infancy, so although a great many organic substances were known, no considerable progress had been made with this branch of chemistry owing to the difficulty of establishing the composition of substances of this class. Dumas, speaking of this time, said, "The nature of most compounds was unknown; their differences, their analogies, their connections had still to be unveiled."

Lavoisier, in the eighteenth century, was one of the first chemists to turn his attention to organic analysis. He burnt a weighed quantity of the organic substance and measured the volume of oxygen required for its combustion. Part of the oxygen united with the carbon of the organic compound to form carbonic anhydride (the volume of which he measured directly) and the remainder with hydrogen to form water, the amount of which he estimated from the quantity of oxygen consumed.

Gay-Lussac and Thenard in 1811 obtained the oxygen required for combustion by burning the organic substance with potassium chlorate. Berzelius improved their method in several ways, but to Liebig belongs the credit of having evolved a method both simple and accurate. He was six years thinking and experimenting, and in 1831, with the invention of his "potash bulbs," perfected the apparatus now in common use in every laboratory. He also devised a new method for estimating nitrogen in organic compounds, invented the well-known Liebig Condenser, and showed how to find the equivalent weight of an organic base by combining its hydrochloride with platinic chloride.

It is impossible to over-estimate Liebig's work on organic analysis as it forms the very foundation of organic chemistry upon which all subsequent work has been built.

When Liebig was quite a boy he became interested in the fulminates, by seeing a cheap-jack in the Market Place at Darmstadt preparing fulminating silver for fire crackers. This interest deepened as he grew older, and in

1822 he published a paper on fulminating mercury. He continued his researches on these most explosive compounds in the laboratory of Gay-Lussac, and finally succeeded in establishing the composition of fulminic acid. Shortly before Wöhler, who was working at Stockholm under Berzelius, had published the result of his analysis of cyanic acid, and Liebig was intensely surprised to find that the result of his analysis of fulminic acid (1823) coincided with that of Wöhler's for cyanic acid.

That two totally dissimilar substances should contain the same elements in the same proportions was so unheard of that Liebig thought Wöhler must have made a mistake and repeated his experiments, but found them quite correct. Gay-Lussac pointed out that the different properties might be due to a different arrangement of the atoms in the molecule. Berzelius at first ridiculed the idea, but as examples multiplied he became convinced and called the phenomenon *isomerism.*

In 1832 Liebig and Wöhler published their classical investigation, "Researches on the Radical of Benzoic Acid." It was known that oil of bitter almonds became converted into benzoic acid on exposure to the air. Liebig and Wöhler showed that this is due to the taking up of oxygen. They prepared a whole series of compounds containing the group $C_{14}H_{10}O_2$ (now written C_6H_5CO) which they called the radical benzoyl.

$C_{14}H_{10}O_2, H_2$	Oil of bitter almonds
$C_{14}H_{10}O_2, O + H_2O$	benzoic acid
$C_{14}H_{10}O_2, Cl_2$	benzoyl chloride
$C_{14}H_{10}O_2, Br_2$	„ bromide
$C_{14}H_{10}O_2, I_2$	„ iodide
$C_{14}H_{10}O_2, Cy_2$	„ cyanide

The discovery of the radical benzoyl was noteworthy because it was the first time a whole series of compounds had been prepared containing a group consisting of three different elements, but its paramount importance lay in the fact that one of these elements was *oxygen*.

Up to this time oxygen had held a unique position amongst the elements. It formed bases by union with the metals, and acids by union with the non-metals, and Berzelius looked upon many organic substances as oxides of organic radicals. Oxygen was held to dominate and to determine the distinctive properties of any molecule in which it occurred, but when Liebig proved that oxygen, associated with two other elements, entered into the composition of a group or radical which passed through a whole series of different compounds, this element was shorn of its kingship and placed on an equality with the other elements.

Lavoisier had familiarised chemists with the name of *radical.* He applied this term to the "residue of a substance which has been deprived of its oxygen," and defined it as "a composite group which behaves like an element." But the first part of this definition became too narrow when Gay-Lussac discovered the radical cyanogen in 1815, followed by Liebig and Wöhler's investigation, "Researches on the Radical of Benzoic Acid" in 1832, neither of which radicals could be defined as the "residue of a substance which has been deprived of its oxygen," and in 1838 Liebig gave the following definition of a compound radical, which is still universally accepted.

"We call cyanogen a radical because it is the never-varying constituent of a series of compounds; because it can be replaced in these by simple bodies; because in its combinations with a simple body, the latter can be separated and replaced by equivalents of other simple bodies. Of these three chief characteristics, two at least must be fulfilled ere it can really be regarded as a compound radical."

Liebig's work on the radical ethyl is of importance. He affirmed that the group C_4H_{10} which he called the radical ethyl, occurs in alcohol and ether, and that alcohol is the hydrate of ether, and ether is an oxide of the radical. He also discovered chloroform, melamine, and other organic substances.

Liebig's friendship with Wöhler was close and lifelong, and the two chemists published many papers in their joint names.

In October, 1836, Wöhler discovered that bitter oil of almonds (benzaldehyde) and prussic acid can be obtained from amygdalin (a substance which occurs in bitter almonds), and suggested that he and Liebig should make a joint research on this subject. They found that bitter and sweet almonds contain a ferment which they called *emulsin*. Amygdalin, under the action of emulsin and in the presence of water, gave benzaldehyde, prussic acid and a sugar (glucose).

Liebig and Wöhler, by this investigation, brought to light the properties of a new class of substances, since called *glucosides*, which are complex organic compounds occurring in vegetable tissues; when hydrolysed with acids or enzymes (inorganised ferments), they all give a sugar, generally glucose.

Uric acid was discovered by Scheele in 1776, but its composition was unknown. Liebig and Wöhler published a joint investigation of this acid in 1838. They succeeded in preparing fifteen derivatives, including alloxan, alloxantin, parabanic acid and oxaluric acid. Their memoir contains the following significant words:—

"From this research the philosophy of chemistry will draw the conclusion that the ultimate synthetical formation in our laboratories of all organic bodies, in so far as they are not organised, may be regarded as not only probable but certain. Sugar, salicin, morphin, will be artificially obtained. As yet we know nothing of the way by which this result is to be attained, inasmuch as the proximate materials for forming these bodies are unknown; but we shall come to know them." This prophecy has not been wholly fulfilled, but E. Fischer has accomplished the synthesis of sugars, and Ladenburg has synthesised the alkaloid coniine.

Liebig showed that many organic acids are polybasic.

Before the importance of his work on this subject can be understood, it will be necessary to briefly consider the views that were previously held.

Vinegar was known to the ancients, and when oil of vitriol and spirits of salt were discovered, they were classified with vinegar as possessing similar properties. Boyle defined acids as substances which are sour in taste, possess considerable power, are able to change many vegetable blues to reds, and act upon alkalies to form neutral substances. Meyer suggested that these properties were due to the presence of a "biting principle," and Stahl thought that they were caused by the presence of a large quantity of "primordial acid," a substance which he believed occurs in smaller quantities in salts and alkalies.

Lavoisier stated that all acids consist of a radical and oxygen (principe acidifiant—principe oxygine), and this view was universally held for some time, but presently this definition was found to be contrary to fact. In 1787 Berthollet showed that hydrocyanic acid contains no oxygen, and Scheele showed that sulphuretted hydrogen, though acid in properties, also contains no oxygen, and Davy demonstrated that hydrochloric acid consists of hydrogen and chlorine only. Gay-Lussac divided acids into two classes, "hydracids," which do not contain oxygen, and "oxyacids," which do.

Dulong and Davy had suggested that hydrogen might be the acidifying principle in acids, and that when a salt is formed a metal takes the place of hydrogen. These views, however, were disregarded, and Berzelius' electro-chemical theory was the one generally held. According to this an acid is an electro-negative oxide, a base an electro-positive oxide, and a salt is formed by the union of these two. Thus sodium sulphate was written $Na\ O.\ S\ O_3$, where $Na\ O$ is the basic or metallic oxide, and $S\ O_3$ the acid or non-metallic oxide. What we now call (acid forming) oxides were then called acids, and what we now call acids were then called hydrates of the acids; thus sulphuric acid was written $S\ O_3.\ O\ H$.

Phosphoric acid was supposed to exist in isomeric forms till Graham, in 1833, discovered metaphosphoric acid, and showed that the various acids are not insomeric but three distinct forms; he also suggested that in the acids water plays the part of a base, and showed that in the salts the ratio of the oxygen of the base to the oxygen of the acid differs in the three acids, and thus introduced the idea of a varying basicity. He wrote the acids thus:

Phosphoric acid	$3HO.PO_5$
Pyrophosphoric acid	$2HO.PO_5$
Metaphosphoric acid	$HO.PO_5$

and the salts of phosphoric acid thus:

$PO_5{\cdot}3NaO$; $PO_5{\cdot}HO{\cdot}2NaO$; $PO_5 2HO{\cdot}NaO$

Liebig visited England in 1837 and was very much impressed with Graham's views regarding the phosphoric acids, and in 1838 Liebig, in conjunction with Dumas, published a memoir on polybasic acids. He examined cyanic, tartaric, citric and other organic acids, and in the same paper revived the theory of acids brought forward by Davy and Dulong, which had fallen into oblivion. In his memoir Liebig gives a very clear statement of the nature of acids and salts, which is held to be correct, in the main, even at the present day, and defined an acid as a compound of hydrogen in which the hydrogen can be replaced by metal, thus abolishing the distinction between hydracids and oxyacids. This view was irreconcilable with the electro-chemical theory of Berzelius, and gradually displaced it.

Agriculture owes an immense debt to Liebig. Although Davy, Boussingault and others had worked at agricultural chemistry, it was still almost unbroken ground when Liebig began his investigations. He took up the work with all his usual energy and thoroughness, and made a tour throughout Germany, England and Scotland to acquaint himself with practical methods. He studied the nutrition of plants and animals, and superintended a factory for the manufacture of mineral manures, which he tested on a plot of ground purchased for that purpose.

His books, "Chemistry in its Applications to Agriculture and Physiology" (1840), "Natural Laws of Husbandry" (1863), and teaching, aroused great interest, and as a result agricultural colleges with experimental farms attached sprang into being on the Continent and in England.

Liebig was great as a teacher, thinker and worker. By his improved methods of organic analysis he laid a firm foundation for this branch of the science. His laboratory at Giessen—the first of the kind—gave an immense impetus to the study of chemistry, since it was speedily followed by the establishment of others, on similar lines, in his own country and elsewhere.

THOMAS GRAHAM

1805-1869

THOMAS GRAHAM was born in Glasgow, December 21st, 1805. His father was a successful manufacturer and gave his son a good education. He entered Glasgow University when he was only fourteen years old, and obtained his M.A. degree five years later.

His father intended Thomas to be a minister in the Scottish Church, but the young man became so interested in science under the teaching of Dr. Thomas Thompson and Meikleham that he wished to devote his life to it, instead of becoming a minister. The elder Graham was very angry, and tried to force his son to comply with his wishes, but in vain, and finally Thomas left home in bitterness, his father refusing to make him any allowance. His mother, however, helped him, and he studied for some time at Edinburgh under Hope and Leslie.

In 1829 he was appointed Lecturer on Chemistry at the Mechanics' Institute in Glasgow, and the following year he was elected to the Lectureship in Chemistry at the Andersonian Institution in the same city. He held this post for seven years, during which time he was made a Fellow of the Royal Society. In 1837 he was appointed Professor of Chemistry in the University of London (now University College). Graham was one of the founders of the Chemical Society in 1841, and also of the Cavendish Society in 1846. He received many honours from foreign Scientific Societies as well as from those of England and Scotland.

In 1854 he was given the appointment of Master of the Mint, and for several years afterwards he was so much occupied with the duties of his office that he was unable to give much time to scientific work.

His health began to decline in 1868, and in the autumn of 1869 he went to Malvern for rest and change. He caught a chill there, which developed into inflammation of the lungs. He recovered sufficiently to return to his home in London, but died there, September 16th, 1869.

Graham's most important work was on the diffusion of gases and liquids.

His first paper on the subject, entitled "A Short Account of Experimental Researches on the Diffusion of Gases through each other, and their separation by Mechanical Means," was published in the "Quarterly Journal of Science," 1829. In these first experiments Graham allowed the gases to escape through a bent capillary tube into the air. The tube passed through a glass stopper into a short graduated cylindrical tube, in which the various gases were placed, first separately and afterwards mixed. He stated that "the diffusiveness of the gases is inversely as some function of their density—apparently the square root of their density." He found that the rate of diffusion of a gas was altered by mixture with other gases.

In 1823 Döbereiner filled a glass jar with hydrogen and left it standing over water. When he returned to it, in about twelve hours, he was surprised to notice that the level of the water inside the jar had risen several inches above the height of that outside. He tried to find the cause of this phenomenon, and found that the glass jar had a small crack in it through which some of the hydrogen had escaped into the air. He varied the experiment by confining hydrogen over water in jars and flasks of different shapes, all having a small crack in the glass, and found that in every case the water rose inside the vessel. However, when ordinary air, nitrogen or oxygen, were used in the same vessels instead of hydrogen, the water did not rise. Döbereiner was not able to give any satisfactory explanation of the phenomenon.

In 1831 Graham turned his attention to this subject, and found that although hydrogen passed outwards through the fissure, a certain amount of air passed inwards. It was impossible to make accurate measurements with the cracked vessels, and Graham soon rejected them.

The apparatus he usually employed consisted of a glass tube from 6 to 14 inches long and half an inch in diameter. This tube, which he called the diffusion tube, was open at one end and closed at the other, with a plug of plaster of Paris about a fifth of an inch in thickness. The tube was graduated into hundredths of a cubic inch. To make the experiment, the tube was filled with gas and inverted over water or mercury. At the end of a given time the volume of gas remaining in the tube was read off, and its composition determined by analysis. From the ratio of air to original gas thus found it was easy to calculate the velocity of diffusion of the given gas compared with the velocity of diffusion of air. Graham stated, as the results of his experiments, " The diffusion rates of any two gases are inversely as the square roots of their densities."

The following table shows the results actually found compared with the numbers calculated according to the above rule.

	By Experiment	$\sqrt{\text{Density}}$
Hydrogen	3.83	3.79
Nitrogen	1.014	1.014
Sulphuretted hydrogen .	.95	.92
Carbon dioxide . . .	.812	.8087

Graham proved that difference of density is not necessary for diffusion, by confining carbon-monoxide and nitrogen (which have the same density) in two vessels separated by a plug of plaster of Paris. At the end of twenty-four hours the gases were uniformly mixed in the two vessels.

In 1846 Graham sent the first part of a memoir on "The Motion of Gases" to the Royal Society, and in 1849 the second part of the same memoir. He gave the name "effusion" to the passage of gases under pressure through a minute aperture (about $\frac{1}{300}$ inch in diameter) in a metallic plate, and states "different gases pass through minute apertures into a vacuum in times which are as the square roots of their respective specific gravities, or with velocities which are inversely as the square roots of their specific gravities—that is, according to the same law as gases diffuse into each other."

He found the same law applied to a mixture of gases, the time of effusion being as the square root of the density of the mixture. Bunsen devised an instrument, based on this law, which gives very accurate results for the specific gravity of gases, and is especially useful when only a small quantity of the gas is available.

Graham found that this rule does not apply to the "transpiration" of gases, the name he gave to the passage of gases through capillary tubes. A "capillary tube" is any tube in which the length is not less than 4,000 times the width.

In the "Philosophical Transactions" for 1863 another paper appears by Graham, "On the Molecular Mobility of Gases." In this paper he describes his latest form of diffusion tube, in which a plate of artificially-compressed graphite, about half a millimeter in thickness, takes the place of the thin plate of plaster of Paris used in his earlier experiments. He says "The pores of artificial graphite appear to be really so minute that a gas *in mass* cannot penetrate the plate at all. It seems that molecules only can pass; and they may be supposed to pass wholly unimpeded by friction, for the smallest pores that can be imagined to exist in the graphite must be tunnels in magnitude to the ultimate atoms of a gaseous body. The sole motive agency appears to be that intestine movement of molecules which is now generally recognised as an essential property of the gaseous condition of matter."

In this memoir Graham describes his tube atmolyser for partially separating the constituents of a mixture of two gases of different densities. The atmolyser consists of a long clay tobacco-pipe stem, surrounded by a wider glass tube fitted with corks at each end, through which the pipe passes. The glass tube is connected with an air pump by means of a short piece of glass tubing passing through one of the corks. The two mixed gases flow slowly down the pipe stem. The lighter gas diffuses through the pipe stem into the glass tube more rapidly than the heavier one and is swept away to the air pump, and the heavier gas, mixed with only a small quantity of the lighter gas, can be collected at the other end of the stem.

Graham studied the movements of liquids as well as gases, and read a paper "On the Diffusion of Liquids" for the Bakerian Lecture to the Royal Society in 1849.

In this paper Graham gives an account of experiments he had made with a view to finding how quickly a salt in aqueous solution diffuses into a layer of pure water above it, but not separated from it in any way.

A bottle of about 4 oz. capacity was nearly filled with a saline solution of known strength, and put inside a glass cylinder. The small bottle was then filled with pure water in such a way as not to disturb the saline solution, and covered with a glass plate. Water was next poured into the outer cylinder to about the depth of an inch above the plate, and the dividing plate then carefully removed. The whole apparatus was kept at a constant temperature for a given number of days, when the small bottle was again covered with the glass plate, removed from the surrounding cylinder, and the strength of its contents determined.

There appears to be no simple relation between the molecular weight of a dissolved substance and its rate of diffusion. The rate of diffusion of a given salt in moderately dilute solution is proportional to the strength of the solution. Solutions of isomorphous salts diffuse at the same rate. Hydrochloric, hydrobromic and hydriodic acids are also equidiffusive. In mixtures of two salt solutions the rate of diffusion of the less soluble salt is retarded.

Graham found it possible by the process of liquid diffusion to almost completely separate some salts into their constituent parts. For example: he separated potassium sulphate and sulphuric acid from a solution of acid potassium sulphate.

In a paper published in the Philosophical Transactions for 1861, Graham describes how liquid diffusion can be applied to analysis. He divides substances into two classes: *crystalloids* are substances which exist in the crystalline form, and when in solution diffuse easily and quickly into water; *colloids* as gums, gelatine, albumen, starch, etc., are substances which are incapable of crystallisation. They are jelly-like in appearance and only diffuse very slowly into water. Colloids cannot diffuse through other colloids, but crystalloids can diffuse through colloids. Graham applied this principle to the separation of crystalloids from colloids, and named the process *dialysis.*

Parchment-paper was found to be the most suitable substance for the colloid septum. This was stretched tightly between two rings or hoops of gutta-percha to form a tambourine-shaped vessel, called the *dialyser.* A solution of the mixed substances was poured inside the dialyser, which was then floated on pure water. Graham, in this way, obtained many substances in the colloidal form that had been unknown before. His process of dialysis is of practical use in the detection of poisons when mixed with considerable quantities of colloidal matter.

Deville and Troost observed that hydrogen will pass through heated plates of platinum and iron, and their experiments led Graham to study the subject of gaseous diffusion through red-hot metallic septa. Hydrogen is apparently the only gas able to penetrate a red-hot plate of platinum. He found that a small volume of hydrogen could be absorbed by copper, gold, silver and iron, at a red heat, and retained after the metals were cold. He called this phenomenon *occlusion*. Palladium can occlude a considerable quantity of hydrogen, even at ordinary temperatures, and at higher temperatures as much as several hundred times its volume of the gas.

Graham's classical memoir "On the Arseniates, Phosphates, and Modifications of Phosphoric Acid," was published in the Philosophical Transactions for 1833. Graham in this paper first clearly defined *basicity*. He also affirmed that hydrogen is an essential constituent of all acids, and discovered metaphosphoric acid.

This chemist was the first to draw a distinction between "water of constitution" and "water of crystallisation," in magnesium sulphate and kindred salts, and he discovered the alcoates as $Ca\ Cl_2\ 4\ (C_2H_5{\cdot}OH)$ in which alcohol is analogous to the water in ordinary crystallised salts.

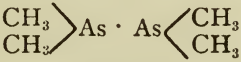
ROBERT WILHELM BUNSEN

1811-1899

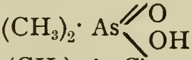
Robert Wilhelm Bunsen was born at Göttingen on March 31st, 1811, where his father was chief University Librarian and Professor of Modern Philology. Young Bunsen's school days were passed at the gymnasium at Holzminden in Hanover. He entered the University at Göttingen in 1828, where he studied chemistry under Stromeyer, the discoverer of cadmium. He obtained his degree in 1830, presenting as his thesis "Enumeratio et descriptio hygrometrorum." He continued his studies in Paris, Berlin and Vienna, and was appointed Privatdozent in Chemistry at the University of Göttingen in 1834. In 1836 he became teacher of chemistry in the Polytechnic School of Cassel In 1839 he went to Marburg and taught in the University there till 1851, when he went for a short time to Breslau. He left here in 1852 to accept the Chair of Chemistry at Heidelberg, which he occupied until 1889, when he retired, though he lived at Heidelberg till his death, in August, 1899.

Bunsen's first great research was the classical one on the cacodyl compounds. In 1760 Cadet had obtained a liquid by distilling potassium acetate with arsenious anhydride. This liquid was poisonous, fuming, spontaneously inflammable, and possessed a very disagreeable smell. The undesirable properties of "Cadet's liquid," as it was called, deterred chemists from trying to find out anything else about it, and it was not until seventy years after its first discovery that Dumas tried to obtain a pure compound from the crude product, which was contaminated with arsenic. Dumas gave the formula $C_8H_{12}As_2$ ($C=6$, $As=75$) to the compound he obtained.

Bunsen turned his attention to the cacodyl compounds in 1837, and continued his investigations for no less than six years. While working at these compounds he lost the sight of his right eye by the explosion of some cacodyl cyanide, and was nearly poisoned, lying for days in a critical condition; but undaunted, he returned to his experiments and carried the investigation to a satisfactory conclusion. Bunsen showed that Dumas' formula was incorrect, and that the pure liquid separated from Cadet's liquid should be represented by the formula $C_4H_{12}As_2O$ (C=12). He called this compound cacodyl oxide. He prepared the chloride, bromide, iodide, cyanide, fluoride, sulphide and cacodylic acid, and finally isolated the radical cacodyl $C_4H_{12}As_2$ which Kolbe subsequently suggested has the constitution



$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle As\cdot As\left\langle\begin{matrix}CH_3\\CH_3\end{matrix}\right.$$

Cacodyl	$\{(CH_3)_2\ As\}_2$
Cacodyl oxide	$\{(CH_3)_2\ As\}_2\ O$
Cacodylic acid	 $(CH_3)_2\cdot As\left\langle\begin{matrix}{/\!/}O\\OH\end{matrix}\right.$
Cacodyl chloride	$(CH_3)_2\ As\cdot Cl$
,, bromide	$(CH_3)_2\ As\cdot Br$
,, iodide	$(CH_3)_2\ As\cdot I$
,, cyanide	$(CH_3)_2\ As\cdot CN$
,, sulphide	$\{(CH_3)_2\ As\}_2.S$

The discovery of the series of cacodyl compounds, and the separation of the cacodyl radical —the first instance of its kind—confirmed the definition of radical enunciated by Liebig as the result of his and Wöhler's investigation of the cyanogen and benzoyl compounds, and may be called one of the foundation stones of the theory of compound radicals.

This important research comprises Bunsen's chief work in the realm of organic chemistry.

Perhaps the most important of all Bunsen's researches was the one on Spectrum Analysis, which he carried out in conjunction with Kirchhoff, Professor of Physics at Heidelberg University.

In 1822 Sir J. Herschel had observed that flames coloured by metallic salts give bright lines, and Swan also drew attention to this phenomenon; and Talbot, in 1834, pointed out that lithia could be distinguished from strontia by means of its spectrum, but Bunsen and Kirchoff were the first to declare that *each* element, in the state of incandescent vapour, gives a *definite* discontinuous spectrum, and to use this fact for the purpose of chemical analysis Bunsen discovered caesium by means of spectrum analysis in 1860—the first element discovered by this method. He first detected this metal in the water of Dürkheim, and called it caesium, from caesius = blue, on account of the two splendid blue lines in its spectrum. The metal occurs in such small quantities in the water that Bunsen only obtained 17 grams of caesium chloride from 40 tons of water.

In 1861 Bunsen discovered rubidium (rubidus = dark red) in the mineral petalite, and worked up 150 kilograms to obtain a small quantity for investigation. Other chemists, inspired by the above research, have looked for new elements with the spectroscope, and their efforts have been rewarded by the discovery of thallium, indium, gallium, and helium.

Bunsen published a valuable account of the spark spectra of the rare earths. He laboured at this tedious and troublesome research for three years, and the finished manuscript was lying on his table ready for publication when it caught fire during his absence from the room, and was totally destroyed. It was a bitter disappointment, but he resolutely set to work to replace his memoir, and completed it for the second time in 1875.

In 1857 Bunsen published a book giving an account of his gasometric researches, and a second and enlarged edition was brought out in 1877. In this book he gives a full description of the eudiometric method of gas analysis which he invented.

The eudiometer consists essentially of a graduated glass tube closed at one end and containing two platinum wires for passing an electric spark. The tube is inverted over mercury. Bunsen used this method to determine the composition of the atmosphere.

He removed traces of ammonia and carbonic acid by means of calcium chloride and caustic potash before introducing the air into the eudiometer. He exploded a known volume of air confined in the eudiometer tube with excess of hydrogen, and noted the diminution of volume. The quantity of water formed was negligible. Since one volume of oxygen unites with two volumes of hydrogen to give water, one third the observed diminution of volume gave the oxygen present in the volume originally taken.

The result of one of Bunsen's experiments was as follows:

Vol: at 0° and 1 m m pressure

428·93	air employed
749·77	after addition of hydrogen
480·09	after the explosion

Diminution = 749·77—480·09 = 269·68
one third of this gives vol. of oxygen $\frac{269\cdot68}{3} = 89\cdot89$

This gives percentage composition
Nitrogen 79·030
Oxygen 20·970
100·000

Modifications of the above method can be used for the analysis of numerous gaseous mixtures.

The book also describes various methods of collecting, preserving and measuring gases ; two new methods for determining the specific gravity of gases with description of a new thermostat ; absorption-coefficients of gases in water and alcohol, determined with a new absorptiometer invented by Bunsen ; gaseous diffusion ; combustion phenomena of gases. Bunsen applied his method of gas analysis to determine the chemical changes which occur in the blast furnace during the preparation of cast-iron. He examined furnaces, both in Germany and England, and made valuable suggestions for recovering bye-products and saving fuel.

This investigation is interesting as being the first attempt to utilise trained scientific knowledge for industrial purposes.

The photochemical researches of Bunsen and Roscoe are extremely important. Ostwald says of them, "In no other research in this domain of science do we find exhibited such an amount of chemical, physical and mathematical dexterity, of ability in devising experiments, of patience and perseverance in carrying them out, of attention given to the minutest detail, or of breadth of view as applied to the grander, meteorological and cosmical phenomena of nature."

Gay-Lussac and Thénard found that hydrogen and chlorine unite with explosive violence in the presence of sunlight, but gradually in diffused daylight. Draper, in 1843, constructed an actinometer based on this property of hydrogen and chlorine. Bunsen and Roscoe greatly improved Draper's apparatus and constructed a very accurate instrument. With this they proved that chemically active rays obey the same laws of reflection and absorption as visible rays, and that their intensity varies inversely as the square of the distance. They found that when a mixture of hydrogen and chlorine was exposed to a constant light, the rate of formation of hydrochloric acid gradually increased during the first nine minutes, and then became constant. They called this phenomenon "photochemical induction."

In addition to all the above, Bunsen invented the burner known by his name; an ice calorimeter; the carbon-zinc battery which bears his name; showed that the electric current could be used for illumination purposes; obtained magnesium in quantity by electrolysis, and showed that the light given by burning magnesium can be used for photographic purposes; invented a photometer; a filter pump; investigated the volcanic phenomenon of Iceland; invented the volumetric method of estimating iodine by sulphurous acid.

Bunsen enriched chemistry by the discovery of new facts and by the invention of useful apparatus; but he did more than this: he opened out new paths and showed new fields for research, where later chemists—many of them his own pupils—won their laurels.

AUGUST WILHELM HOFMANN

1818-1892

AUGUST WILHELM HOFMANN was the son of an architect, and was born at Giessen, April 8th, 1818.

August devoted his first years at College to the study of law and philology, and does not appear to have taken any interest in chemistry. But it so happened that his father was entrusted with the preparation of the plans for Liebig's new laboratory at Giessen, and owing to this circumstance young Hofmann became acquainted with that eminent chemist. August at once took up the study of chemistry, and in course of time became one of Liebig's assistants. He remained with Liebig until 1845, when he went to Bonn.

Liebig came to England in 1842 to investigate agricultural methods, and made a tour throughout England and Scotland, and meetings were held in many places at which he spoke on agricultural chemistry. In consequence of this tour chemistry became popular and laboratories were in great demand, and in 1845, chiefly owing to the efforts of the Prince Consort and Sir James Clark, the Royal College of Chemistry was founded. This College was intended primarily for students who wished to devote themselves to research work and to study chemistry for its own sake. Hofmann was asked to be the first director of this College, and he commenced work in London in 1845. Some years afterwards, when popular enthusiasm was beginning to wane and subscriptions to the Royal College were dwindling, Hofmann succeeded Lyon Playfair as Professor in the School of Mines, and the Royal College became amalgamated with this institution.

Hofmann left England in 1864 and returned to Bonn, but he did not remain there long, as the next year he succeeded Mitscherlich as Professor of Chemistry in Berlin University.

Hofmann was married four times and died suddenly at Berlin, May 5th, 1892.

He was elected a Fellow of the Royal Society in 1851, and was awarded the Copley Medal in 1875.

The researches of Hofmann and his pupils had a great influence on industrial development, especially on the coal-tar industry, which was brought into existence as the result of his work.

W. H. Perkin, one of Hofmann's pupils, and the first to manufacture an aniline dye, "mauve," on the technical scale (1856) speaks thus: "This industry has directly and indirectly had a most marvellous influence on the advancement of chemical science, especially that part of it relating to the aromatic series of compounds. No other industry in existence can at all be compared with it from this point of view, . . . as it has utilized the discoveries of chemists, it has handed back to them in return new products which they could not have obtained without its aid, and these have served as materials for still more advanced work: This kind of exchange, indeed, has been going on so repeatedly that products formerly of the rarest and most complex character are now quite common substances in the coal-tar colour works."

Hofmann's first investigation was conducted in Liebig's laboratory at Giessen, and concerned "Organic bases contained in coal-gas naptha."

Unverdorben in 1826 obtained a substance by the dry distillation of indigo, which he called "crystalline." Runge in 1834 found a compound in coal-tar which gave a violet-blue coloration with chloride of lime, and called it "kyanol." Fritzshe in 1841 distilled indigo with potash, and obtained a substance which he called "aniline. Zinin in 1842 obtained "benzidam" by reducing an alcoholic solution of nitrobenzene with sulphuretted hydrogen in the presence of ammonia. Hofmann, in 1843, showed that all the above substances are identical and adopted the name *aniline.* In his paper he gave an account of the properties of aniline, its most important reactions, and a description of its salts.

In 1845 Hofmann published a paper "On the metamorphoses of Indigo. Production of Organic Bases which contain Chlorine and Bromine."

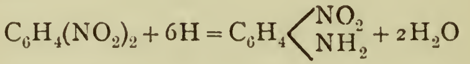
Some years before this Laurent had stated that in many organic compounds chlorine can be substituted for equivalent quantities of hydrogen without sensibly altering the properties of the original compound. Berzelius refused to accept this statement, because if true, it struck a deadly blow at his electrochemical theory, and a wordy war ensued between these two chemists and their respective partisans.

Several compounds were known—notably trichloracetic acid—in which substitution had taken place without causing any great change of properties, but up to 1845 no organic base was known in which the hydrogen had been replaced by chlorine without destroying the basic properties of the compound. Tribromaniline prepared by Fritzshe was a neutral substance, but Hofmann thought it possible that if only *one* equivalent of hydrogen could be replaced by chlorine or bromine, the basic properties of aniline might persist ; so he set to work to try to prepare these compounds. He remembered that Fritzshe obtained aniline by distilling indigo with potash, also that isatin is a product of the oxidation of indigo, and therefore would probably be converted into indigo by fusion with potash, and if so, chlor and dichlor isatin would probably give chlor and dichlor aniline by fusion with potash, and this surmise turned out to be correct. He sums up his results in the following words:

"It appears, however, that the chlorine preserves, to a certain extent, its electro-negative character in those compounds in which it replaces hydrogen, and that in proportion to the increase in the number of equivalents of the latter, for which chlorine or bromine are substituted, so is this character the more impressed on the resulting compounds. The compound atom aniline, $C_{12}H_7N_1$, in consequence of the peculiar arrangement of its elements, possesses the property of uniting with an acid; replace one equivalent of its hydrogen by bromide and we obtain bromaniline, a body possessing likewise basic properties but in a feebler degree, . . . substitute now another equivalent of bromide for hydrogen, and we have dibromaniline. The facility with which all its salts are decomposed evidently indicates that the basic character of aniline is further enfeebled by the repeated assumption of bromine. Finally, in tribromaniline the electro-negative properties of the assumed bromine equivalent s have placed themselves in equilibrium with the electro-positive character of the original system."

Liebig, commenting upon this paper, said: "It appears to me that he (Hofmann) has produced a definite and irrefrangible proof that the chemical character of a compound does not depend, as the electro-chemical theory supposes, upon the *nature* of the elements it contains, but solely on the manner of their grouping."

In 1846 Hofmann and Muspratt obtained nitraniline by the partial reduction of dinitrobenzene.



$$C_6H_4(NO_2)_2 + 6H = C_6H_4\left\langle\begin{matrix}NO_2\\NH_2\end{matrix}\right. + 2H_2O$$

"Researches on the Volatile Organic Bases" appeared in 1848. This paper gives an account of melaniline (diphenylguanidine), etc.

All alkaloids (organic bases) were supposed by Berzelius to be conjugated ammonia compounds, and Hofmann at one time supported this view and wrote aniline $C_{12}H_4(NH_3)$ $[C = 6]$ as a compound of ammonia NH_3 with the conjunct $C_{12}H_4$. Liebig, however, regarded aniline as a compound of amide (N_2H_4) with the radical $C_{12}H_{10}$ and wrote aniline $C_{12}H_{10}N_2H_4$. To Hofmann belongs the credit of settling this important question.

According to Berzelius oxalate of aniline should be written $\left\{NH_3(C_{12}H_4)\right\}_2H_2C_2O_4$. Now oxalate of ammonia is written $(NH_3)_2H_2C_2O_4$, and by withdrawing four equivalents of water from this salt, cyanogen $(C\,N)_2$ is obtained. If Berzelius' formula is correct for oxalate of aniline, it should be possible to deprive this salt also of four equivalents of water to give an analogous compound to cyanogen, namely *anilo*nitrile $\left\{C_{12}H_4{\cdot}CN\right\}_2$ but this cannot be done, which is in perfect accord with the formula $\left\{(C_{12}H_5)\,NH_2\right\}_2H_2C_2O_4$ for aniline exalate. For it can plainly be seen that it is impossible to withdraw four molecules of water from the salt represented by this formula without destroying the group $C_{12}H_5$. Hofmann says: "The apparent impossibility of obtaining an anilocyanogen throws some doubt on the pre-existence of ammonia in aniline. It is probable more in conformity with truth to consider aniline as a substitution product, as ammonia in which part of the hydrogen is replaced by phenyl. . . . A series of researches on the action of the bromides of the alcohol radicals on aniline and on ammonia have enabled me actually to replace the basic hydrogen of these substances, equivalent, for equivalent by the alcohol radicals, and to produce in this manner numerous series of new alkaloids which appear to admit of no other mode of interpretation."

Gautier was the first to prepare isocyanides by heating an alkyl iodide with silver cyanide. Hofmann—ignorant of this chemist's discovery—soon afterwards, (1869) accidently came upon another way of preparing these compounds.

Prussic acid is formed when ammonia acts upon chloroform at a high temperature under pressure

$$CHCl_3 + NH_3 = HCN + 3HCl$$

but the experiment is not a suitable one for a lecture platform. Hofmann thought if he added potash to the mixture to fix the HCN as soon as formed, the reaction might proceed more rapidly; he found this to be the case, and subsequently tried various primary amines instead of ammonia. He "was astonished to observe in each case a powerful reaction, giving rise to the evolution of vapours of an almost overwhelming odour, strongly recalling that of prussic acid. But few experiments were necessary for the purpose of isolating the odoriferous body. The compounds thus formed are the substances isomeric with the hydrocyanic ethers or nitriles hitherto examined."

Würtz in 1848 was the first to obtain methylamine and ethylamine by distilling the corresponding isocyanates with potash.

$$O{:}C{:}N.C\,H_3 + 2K\,O\,H = N\,H_2\,.C\,H_3 + K_2C\,O_3$$

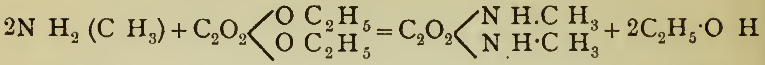
methylisocyanate methylamine

$$O{:}C{:}\,N.C_2H_5 + 2K\,O\,H = N\,H_2\,.C_2H_5 + K_2C\,O_3$$

ethylisocyanate ethylamine

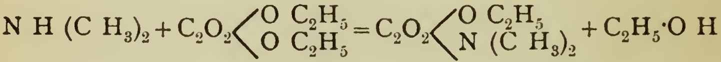
This discovery attracted an immense amount of attention, and these substances (like aniline) were regarded by the followers of Berzelius as conjugated ammonia compounds $N\,H_3.C\,H_2$ $NH_3.C_2H_4$ and by the followers of Liebig as amidogen compounds (N_2H_4 = amide)

Hofmann showed that the amines can also be prepared by heating alkyl chlorides, bromides or iodides in closed vessels with alcohol saturated with ammonia. Not only the primary compounds are formed in this way, but also the secondary and tertiary. Hofmann devised the following method for separating and purifying these products. Treat the mixture of the dry bases with diethyloxalate, the reaction is as follows :



$$2NH_2(CH_3)+C_2O_2\Big\langle\begin{array}{l}OC_2H_5\\OC_2H_5\end{array}=C_2O_2\Big\langle\begin{array}{l}NH.CH_3\\NH\cdot CH_3\end{array}+2C_2H_5\cdot OH$$

methylamine diethyloxalate dimethyloxamide alcohol

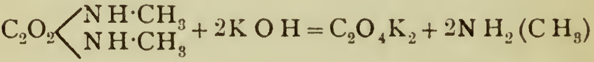


$$NH(CH_3)_2+C_2O_2\Big\langle\begin{array}{l}OC_2H_5\\OC_2H_5\end{array}=C_2O_2\Big\langle\begin{array}{l}OC_2H_5\\N(CH_3)_2\end{array}+C_2H_5\cdot OH$$

dimethylamine dimethylethyloxamate

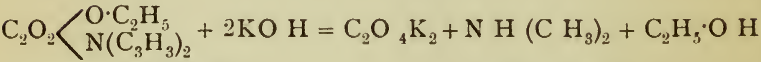
Trimethylamine is not acted upon, and can be obtained by distillation.

The oxamide is soluble in water while the oxamate is insoluble, hence the former can be extracted by digesting with water. The oxamide and oxamate are then separately distilled with potash.



$$C_2O_2\Big\langle\begin{array}{l}NH\cdot CH_3\\NH\cdot CH_3\end{array}+2KOH=C_2O_4K_2+2NH_2(CH_3)$$

dimethyloxamide potassium oxalate methylamine



$$C_2O_2\Big\langle\begin{array}{l}O\cdot C_2H_5\\N(C_3H_3)_2\end{array}+2KOH=C_2O_4K_2+NH(CH_3)_2+C_2H_5\cdot OH$$

dimethylethyloxamate dimethylamine

Hofmann showed that *primary* amines give isonitriles (recognised by their objectionable odour) when warmed with alcoholic potash and chloroform.

$$CH_3NH_2+CHCl_3+3KOH=CH_3\cdot N:C+3KCl+3H_2O$$

methylamine chloroform methylisonitrile

This chemist discovered the compounds known as the quaternary bases, by warming an anhydrous mixture of ethyl iodide and triethylamine. He performed the experiment without much hope of any result, and the crystalline product formed $N(C_2H_5)_4I$ was somewhat of a surprise to him. He examined it with very great interest, and found that it could not be decomposed by distilling with potash, that it broke up on heating into triethylamine and ethyl iodide, and was converted by moist silver oxide into the hydroxide $N(C_2H_5)_4.OH$ closely resembling the caustic alkalis. He says: "The molecular group combined with iodine ... behaves like sodium or potassium: it is a true organic metal in all its bearings. For this metal, I propose, on the ground of its formation and composition, the name tetrethylammonium, which implies that it is built up by the intimate union of nitrogen with four equivalents of the hypothetical hydrocarbon ethyl, and that it may be viewed as ammonium in which the whole of the hydrogen is replaced by an equivalent proportion of the above hyrdocarbon."

Thénard in 1846 discovered the tertiary

phosphines $P\ R_3$, in which R represents an alkyl radical. Hofmann and Cahours fully investigated these compounds in 1855 and their reactions, and compared them with the corresponding compounds of arsenic, antimony and nitrogen, and showed that they will all unite with a molecule of an alkyl iodide to give quaternary salts, which all react with moist silver oxide to give strongly basic hydroxides

$$M\ R_3 + R\ I = M\ R_4I$$
$$M\ R_4I + AgO\ H = M\ R_4{\cdot}O\ H + Ag\ I$$

where M = nitrogen phosphorus, arsenic or antimony, and R = an alkyl radical.

Later, Hofmann prepared the beautiful red crystalline compound $P(C_2H_5)_3\ C\ S_2$ by bringing together triethyl phosphine and carbon bisulphide, and showed that the reaction is so delicate that it can be used as a test for minute quantities of carbon bisulphide.

Although the tertiary compounds had been known for so long, it was not until 1871 that Hofmann was able to prepare primary and secondary phosphines, by heating a mixture of phosphonium iodide, zinc oxide, and an alcoholic iodide to about 150°

$$2\ PH_4I + 2\ C_2H_5I + ZnO = 2\ \underset{\text{ethylphosphine}}{P(C_2H_5)\,H_2{\cdot}HI} + ZnI_2 + H_2O$$

$$PH_4I + 2\ C_2H_5I + ZnO = \underset{\text{diethylphosphine.}}{P(C_2H_5)_2\,H{\cdot}HI} + ZnI_2 + H_2O$$

He showed that the salts of primary phosphines are decomposed by water, and the salts of secondary phosphines by potash. He prepared the two methyl, ethyl, isopropyl, isobutyl and isoamyl phosphines; also the two benzyl phosphines, by using benzyl chloride. He subsequently gave an account of many mixed phosphines, and phosphonium derivatives.

Hofmann published many papers on the polyammonias, and prepared  $C_2H_4\!\left\langle\begin{matrix}NH_2\\NH_2\end{matrix}\right.$ ethylene diamine, $C_6H_4(NH_2)_2$ phenylene diamine, and many other polybases.

Benzene was discovered by Faraday in 1825, and was shown to be present in coal-tar by Hofmann in 1845.

Hofmann and Cahours, in 1856, discovered allyl alcohol $CH_2{=}CH.CH_2.OH$, which was the first example of an unsaturated alcohol. They prepared many of its derivatives, including the sulphide, which they showed to be identical with oil of garlic, obtained from the plant known by that name (Allium sativum). The unsaturated acid, sorbic acid $C_6H_8O_2$, was first prepared by these two chemists from the volatile oil obtained on distilling unripe mountain ash berries with steam.

Hofmann had often wished to prepare methyl aldehyde because he "sadly missed" the first member of the aldehyde series when lecturing on these compounds. In 1869 his desire was gratified, and he obtained formaldehyde in solution by passing the vapour of methyl alcohol mixed with atmospheric air over a red-hot platinum spiral. On treating the solution with sulphuretted hydrogen he was able to separate a crystalline compound that on analysis proved to be $C\ H_2S$. He did valuable work on the isocyanates and mustard oils, discovered paratoluidine and hydrazo-benzene, was the first to use a metal together with an acid as a reducing agent, and pointed out the power of "nascent" hydrogen; determined the correct formula $C_{18}H_{12}$ $[C = 6]$ for mesitylene, found the density of quinone, suggested the present nomenclature of the hydrocarbons, namely the suffix *ane* for the methane series, *ene* for the ethylene series, etc., and invented the apparatus for determining vapour density which bears his name.

He discovered that many beautiful dyes can be prepared by the action of methyl, ethyl and amyl iodides on rosaniline, and patented the process for preparing these colouring matters in 1863; afterwards he produced other dyes by various processes. His researches on colouring matters extended from 1862 to 1887, and during this period he published many memoirs on dyes and substances produced during their preparation.

LOUIS PASTEUR
1822-1895

Louis Pasteur was born at Dôle, 27th December, 1822. His father was a tanner, and removed to Arbois when his son was two years old. Louis studied at the Collège Communal at Arbois, and afterwards at Besançon, where he obtained his degree of Bachelier ès Lettres. In 1843 he entered the École Normale at Paris, and had the privilege of attending the lectures of Balard there, and of Dumas at the Sorbonne. When he had completed his course he was engaged as assistant to M. Balard. In 1848 he was appointed Professor of Physics at the Lycée at Dijon, and three months later became Deputy-Professor of Chemistry at the University of Strasburg, and Professor in 1852. He married in 1850. On the day appointed for the ceremony he became so engrossed in his experiments that he forgot all about his wedding, and had to be fetched by one of his friends! Notwithstanding this unfortunate beginning, the marriage proved a very happy one. He died 1895.

Pasteur's chief chemical work was on optically active substances, especially the tartrates.

Probably owing to a friendship he formed with M. Delafosse, who had studied under Haüy, Pasteur became interested in crystallography at the very beginning of his career, and as soon as he had finished his course at the École Normale, he began work on the crystalline form of the tartrates.

It was known that some solids as quartz, and some liquids as tartaric acid, sugar, etc., possess the power of rotating a ray of polarised light. Haüy had noticed small facets on quartz crystals, and also that the facets varied in position, and had divided quartz crystals into right-handed and left-handed quartz according to the side on which the facets appeared. Biot found that the plane of polarisation was rotated to the right by some crystals of quartz, and to the left by others, and Sir J. Herschell, in 1820, suggested that the different rotations depended upon the different positions of the facets in the crystals.

Tartaric acid and its salts were known to be active, and racemic acid and its salts inactive.

These theories and observations made a great impression on Pasteur, and during his investigation of the crystalline form of the tartrates he noticed that tartaric acid, and also its salts, crystalise with facets (hemihedral faces), a fact that had escaped the notice of all previous investigators. He examined crystals of racemic acid and its salts (optically inactive), and found that these crystals have no hemihedral faces. He next prepared some sodium ammonium racemate (optically inactive), and expected that, like racemic acid, the crystals would have no facets, but there they were! Surprised and perplexed, he examined the crystals with the greatest care, and soon noticed that the facets on some of them were turned to the right, and on others to the left. He separated the two kinds of crystals into two groups, dissolved each group in water, and examined the separate solutions in the polarimeter, and found that the solution of the right-handed crystals rotated the plane of polarisation to the right, and the solution of the left-handed crystals to the left.

In this way Pasteur split up racemic acid into tartaric acid (dextro-rotatory), and an acid hitherto unknown, laevo-tartaric acid. He showed that these two acids have precisely the same chemical and physical properties, with the exception of the different hemihedral faces and optical properties. He also showed that racemic acid could be regenerated by mixing concentrated solutions of l. and d. tartaric acids. The following are extracts from lectures delivered by Pasteur before the Chemical Society of Paris, 1860, showing the inferences he drew from his discovery.

"In isomeric bodies the elements and the proportions in which they are combined together are the same, the arrangement of the atoms is alone different. The great interest attaching to isomerism lies in the introduction of the principle that bodies can be and really are distinct, through possessing different arrangements of their atoms within their molecules."

"We know . . . that the molecular arrangements of the two tartaric acids are asymmetric, . . . and that these arrangements are absolutely identical, excepting that they exhibit asymmetry in opposite directions. Are the atoms of the dextro-acid grouped in the form of a right-handed spiral, or are they placed at the apex of an irregular tetrahedron, or are they disposed according to this or that asymmetric arrangement? We do not know. But there can be no doubt that we are dealing with asymmetric arrangements which are not superposable."

Pasteur did not rest satisfied with the results he had already achieved, but set to work to devise other means of splitting up racemic compounds into their active constituents.

When l. and d. tartaric acids are combined with inactive bases as soda, lime, baryta, etc., the salts of the two acids have similar physical properties, but when l. and d. tartaric acid are combined with optically active bases, this similarity is no longer seen, and the two series of salts have different solubilities, crystalline form, etc. Pasteur thought it highly probable that an active base would have power to split up a racemic compound in the act of forming the two different salts (l. and d.) He found this was the case and says: "Many are the abortive attempts which I have made in this direction, but I have at length achieved success with the assistance of two new isomeric bases quinicine and cinchonicine, which I can very easily obtain from quinine and cinchonine respectively. I prepare the cinchonicine racemate by first neutralising the base and then adding as much acid again. The first crystals to separate are perfectly pure cinchonicine laevo-tartrate. The whole of the dextro-tartrate remains in the mother liquor as it is more soluble; gradually this also crystallises out, but in forms which are totally distinct from those of the laevo-tartrate."

This method, viz., the resolution of racemoid compounds into d. and l. constituents by combination with an active acid or base and fractional crystallisation, has been of the greatest service to chemists. It was used by Ladenburg in his synthesis of coniine, and by Emil Fischer in his synthesis of sugars, both researches of the highest interest and importance.

Pasteur was the originator of yet another method of splitting up racemic compounds.

Solutions of calcium tartrate often undergo fermentation in warm weather, and one day Pasteur noticed that this process had taken place in a solution in his laboratory, and the incident made him curious to find out how a salt of racemic acid would be affected by fermentation. He thus describes the result of his experiment with ammonium racemate.

"The initially inactive liquid becomes perceptibly laevorotatory, and this rotation gradually increases and attains a maximum. The fermentation is then interrupted. There is now no trace of the dextrotartaric acid left in the liquid, which on being evaporated and treated with an equal volume of alcohol yields a fine crop of crystals of ammonium laevotartrate."

This method has been extremely useful, as almost all racemoid substances can be split up into their two constituents by a suitable organism, usually a yeast, mould, or some kind of bacteria.

In 1853 Pasteur obtained mesotartaric acid by heating d. tartaric acid with water. He found that this acid was inactive but quite distinct from racemic acid, and that it could not be split up into d. and l. forms.

The following extracts testify to the worth of Pasteur's work in the eyes of his fellow-chemists. Frankland says:

"Pasteur's work . . . forms, not only the foundation, but nearly the whole of the framework on which that great structure of stereochemistry has been subsequently raised."

Emil Fischer says:

"If we look back to-day on this wide domain (optical activity) we are forced to admit that notwithstanding the large number of new observations, and notwithstanding all the advances in detail that have been made, there is hardly a new fact of fundamental importance which has been added to his discoveries"

Professor Japp:

"Of the numerous weighty discoveries which science owes to the genius of Pasteur, none appeals more strongly to chemists than that with which he opened his career as an investigator —the establishing of the connection between optical activity and molecular asymmetry in organic compounds. The extraordinary subtlety of the modes of isomerism then for the first time disclosed; the novelty and refinement of the means employed in the separation of the isomerides, the felicitous geometrical hypothesis adopted to account for the facts—an hypothesis which subsequent investigation has served but to confirm, the perfect balance of inductive and deductive method; and lastly, the circumstance that in these researches Pasteur laid the foundation of the science of stereochemistry : these are characteristics, any one of which would have sufficed to render the work eminently noteworthy, but which, taken together, stamp it as the capital achievement of organic chemistry."

Pasteur did valuable work in other branches of science. He made most exhaustive researches on fermentation, and came into conflict with Liebig on this subject.

Pasteur maintained that fermentation is due to the vital processes of *living* organisms, while Liebig considered it merely a chemical change induced by the putrefaction of *dead* organisms.

Pasteur also investigated the vinegar process, brewing, and the diseases of wines, and his researches on anthrax and rabies are of world-wide renown.

ALEXANDER WM. WILLIAMSON

1824-1904

ALEXANDER WILLIAM WILLIAMSON was born at Wandsworth, on May 1st, 1824. He was very delicate as a child, and though his general health improved as he grew older, his left arm had little use in it throughout his life, and he lost the sight of his right eye before he reached manhood.

His father, who was a clerk in the East Indian House, retired on a pension about 1840, and went to live in Germany. He wished his son to be a doctor, and in 1840 entered him as a student in the University of Heidelberg to prepare for that profession. But young Williamson became so interested in chemistry, under the excellent tuition of Leopold Gmelin, that he decided to be a chemist instead of a doctor.

In April, 1844, Williamson went to the

University of Giessen, and remained there two years. He studied chemistry under Liebig until the autumn of 1845, when he abandoned chemistry for a time to work at mathematics and physics. In 1846 he went to Paris to study advanced mathematics under Comte, but he still worked at chemistry in a little private laboratory which he had established in his own house.

In 1849 he met Graham, and the same year he became Professor of analytical and practical chemistry in University College, London, where Graham was Professor of Chemistry. In 1855 Graham resigned his professorship, and Williamson took his Chair in addition to his own. He held both appointments until 1887, when he retired, and went to live at Hindhead near Haslemere.

He married Emma Key in 1855, and died at Hindhead, May 6th, 1904. He was elected a Fellow of the Royal Society in 1855 and received honours from many British and Foreign Scientific Societies.

Williamson's most important work was on the ethers. He enunciated the present theory of etherification and established it by a series of brilliant experiments.

In 1850 Williamson attempted to synthesise the higher homologues of alcohol. He dissolved metallic potassium in absolute alcohol to form potassium ethylate, and then acted upon this compound with ethyl iodide. He expected that ethyl would take the place of potassium, and that the product would be an ethylated ethyl alcohol; but instead of a new alcohol he only obtained the well-known ordinary ether. But although he had failed in his endeavour to synthesise a new alcohol, his attempt had given him the key to the composition of ether.

Liebig had put forward the theory that ether is the oxide, and alcohol the hydrated oxide of ethyl

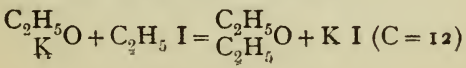
$C_4H_{10}O$	$C_4H_{12}O$	$(C = 12.\ O = 16)$.
ether	alcohol	

Gerhardt and Laurent considered the formulae should be

C_2H_6O	$C_4H_{10}O$
alcohol	ether

but Liebig's formulae were the ones generally accepted until Williamson proved that Gerhardt and Laurent's were correct.

Williamson wrote his equation



$$\begin{matrix}C_2H_5\\K\end{matrix}O + C_2H_5\ I = \begin{matrix}C_2H_5\\C_2H_5\end{matrix}O + K\ I \quad (C = 12)$$

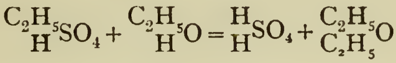
He next prepared mixed ethers; methyl ethyl ether, and ethyl amyl ether, and showed that the same ether resulted from using ethyl alcohol and methyl iodide as from using methyl alcohol and ethyl iodide. He concluded from his experiments that ether is derived from alcohol by replacing a hydrogen atom in the latter by ethyl.

In addition to solving the constitution of ether, Williamson explained the course of the reaction when it is formed by treating alcohol with sulphuric acid.

The first theory was that the sulphuric acid acts simply as a dehydrating agent; later, Berzelius, and then Mitscherlich, suggested that sulphuric acid decomposes alcohol into ether and water by contact, and takes no part in the reaction (calalytic action). Liebig showed that ethyl sulphuric acid is formed before ether, and that therefore the action of the sulphuric acid could not be catalytic.

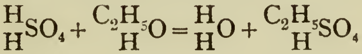
He supposed that ethyl sulphuric acid breaks up when heated into ether and sulphuric acid, but Graham (1850) showed that ethyl sulphuric acid only gives ether when heated with alcohol, and not when heated alone, even to 140°.

Williamson explained the formation of ether from ethyl sulphuric acid by the following equation, which is still held to be correct.



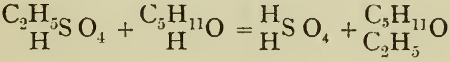
$$\begin{matrix}C_2H_5\\H\end{matrix}SO_4 + \begin{matrix}C_2H_5\\H\end{matrix}O = \begin{matrix}H\\H\end{matrix}SO_4 + \begin{matrix}C_2H_5\\C_2H_5\end{matrix}O$$

and the formation of ethyl sulphuric acid by



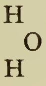
$$\begin{matrix}H\\H\end{matrix}SO_4 + \begin{matrix}C_2H_5\\H\end{matrix}O = \begin{matrix}H\\H\end{matrix}O + \begin{matrix}C_2H_5\\H\end{matrix}SO_4$$

To confirm his statements he acted on ethyl sulphuric acid with amyl alcohol, and obtained the expected ethyl amyl ether.

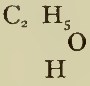


$$\begin{matrix}C_2H_5\\H\end{matrix}S\,O_4 + \begin{matrix}C_5H_{11}\\H\end{matrix}O = \begin{matrix}H\\H\end{matrix}S\,O_4 + \begin{matrix}C_5H_{11}\\C_2H_5\end{matrix}O$$

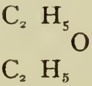
He showed that alcohol and ether could be referred to the type water.



$$\begin{matrix}H\\O\\H\end{matrix}$$

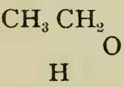


$$\begin{matrix}C_2\,H_5\\O\\H\end{matrix}$$



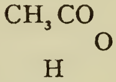
$$\begin{matrix}C_2\,H_5\\O\\C_2\,H_5\end{matrix}$$

He was of the opinion that acetic acid is derived from alcohol by replacing two atoms of hydrogen of the ethyl group by oxygen.



$$\begin{matrix}CH_3\,CH_2\\O\\H\end{matrix}$$

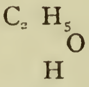
alcohol



$$\begin{matrix}CH_3\,CO\\O\\H\end{matrix}$$

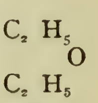
acetic acid

He called the group $C_2\,H^3\,O$ othyl, and pointed out that if one of the hydrogen atoms in acetic acid could be replaced by othyl, a compound would result which would bear the same relation to acetic acid that ether does to alcohol.



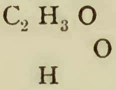
$$\begin{matrix} C_2H_5 & \\ & O \\ H & \end{matrix}$$

alcohol



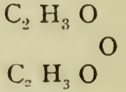
$$\begin{matrix} C_2H_5 & \\ & O \\ C_2H_5 & \end{matrix}$$

ether



$$\begin{matrix} C_2H_3O & \\ & O \\ H & \end{matrix}$$

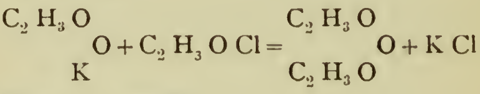
acetic acid



$$\begin{matrix} C_2H_3O & \\ & O \\ C_2H_3O & \end{matrix}$$

acetic anhydride

Such a compound was prepared subsequently by Gerhardt by treating potassium acetate with acetyl chloride.



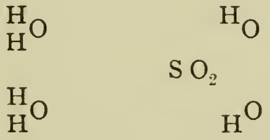
$$\begin{matrix} C_2H_3O & \\ & O \\ K & \end{matrix} + C_2H_3OCl = \begin{matrix} C_2H_3O & \\ & O \\ C_2H_3O & \end{matrix} + KCl$$

potassium acetate acetyl chloride

Williamson's investigations on the formation of ether were of great importance with regard to molecular weight determinations, as they showed that the constitution of a molecule of a substance (and hence its molecular weight) can often be determined by purely chemical means.

In 1851 Williamson published a paper "On the Constitution of Salts," in which he referred a great many substances to the water type, and said, "I believe that throughout inorganic chemistry, and for the best known organic compounds, one single type will be found sufficient: it is that of water, represented as containing two atoms of hydrogen to one of oxygen, thus $\begin{matrix}H\\H\end{matrix}O$. In many cases a multiple of this formula must be used, and we shall presently see how we thereby get an explanation of the difference between monobasic and bibasic acids."

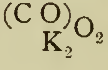
He looked upon sulphuric acid as derived from two molecules of water by the replacement of two atoms of hydrogen by the dibasic group, $S\,O_2$



$$\begin{matrix} \begin{matrix}H\\H\end{matrix}O & \qquad & \begin{matrix}H\\ \end{matrix}O \\ & & S\,O_2 \\ \begin{matrix}H\\H\end{matrix}O & & \begin{matrix} \\ H\end{matrix}O \end{matrix}$$

and therefore regarded sulphuric acid as a dibasic acid.

He applies the same idea to potassium carbonate and says:

" One atom of carbonic oxide is here equivalent to two atoms of hydrogen, and by replacing them, holds together the two atoms of hydrate in which they were contained, thus necessarily forming a bibasic compound  $\begin{matrix}(C\,O)\\K_2\end{matrix}O_2$ carbonate of potash."

EDWARD FRANKLAND

1825-1899

EDWARD FRANKLAND was born at Churchtown, Lancashire, January 18th, 1825. His mother and stepfather removed to Lancaster when he was about seven years old, and he attended a private school there until he was twelve, when he entered the Lancaster Grammar School, where he remained until he was fifteen.

Edward became interested in Science at a very early age, and had read books on chemistry and Priestley's book on Electricity before he was twelve years old.

When he left school he was apprenticed to a druggist in Lancaster, who worked him very hard and did not try to help him with his studies. Fortunately he became acquainted with Dr. James Johnson, who had a laboratory fitted up, in which he allowed Frankland and other druggists' apprentices to work in the evenings.

Frankland entered Playfair's laboratory in 1845, and soon afterwards Playfair made him one of his assistants in the College for Engineers, Putney, and early in 1874 he promoted him to the position of chief assistant.

In May of the same year Frankland and Kolbe, another of Playfair's assistants, went to Marburg for a few months to work under Bunsen. Frankland returned in the autumn to take up the post of lecturer in botany, chemistry and geology at Queenwood College, Hants, but went back to Marburg in October, 1848, and took his Ph.D. degree there in 1849. The following August he went to Giessen to work in Liebig's laboratory, and remained there until Christmas. Next year he was appointed to succeed Playfair at Putney, but left in January, 1851, to become Professor of Chemistry in the newly founded Owens College, Manchester. He married Fräulein Fick the same year.

In October, 1857, he became lecturer on chemistry in St. Bartholomew's Hospital, London, and in 1863 Professor of Chemistry in the Royal Institution. In 1865 he succeeded Hofmann at the Royal College of Chemistry and Royal School of Mines. He held this post until he retired in 1885. He died in Norway, August 9th, 1899, some months after the death of his second wife, Miss Ellen Frances Grenside. He was made a Knight in 1897, and was the recipient of many chemical honours, including Fellowship of the Royal Society (1853).

It was in 1848, when working in Bunsen's laboratory at Marburg, that Frankland succeeded in isolating hydrocarbons of the methane series, which were at first supposed to be free alcohol radicals. He obtained, as he thought, the free radical methyl CH_3 by heating methyl iodide with zinc. Kolbe obtained the same gas by decomposing acetic acid with the electric current. In accordance with Avogadro's Law the formula for the gas was afterwards doubled $\left.\begin{matrix}C\,H\\C\,H_3\end{matrix}\right\}$ and the name changed to dimethyl.

Würtz prepared mixed radicals by the action of sodium on two different alkyl iodides. For example $\left.\begin{matrix}C_2H_5\\C_5H_{11}\end{matrix}\right\}$ ethyl-amyl.

Frankland obtained a gas by heating ethyl iodide with zinc and water, which he called hydride of ethyl $\left.\begin{matrix} C_2H_5 \\ H. \end{matrix}\right\}$

It was thought that the homologues of marsh gas formed two series.

(1) Two radicals united to form a molecule e.g., $\left.\begin{matrix} CH_3 \\ CH_3 \end{matrix}\right\}$

(2) A radical united with an atom of hydrogen (the hydrides) e. g., $\left.\begin{matrix} C_2H_5 \\ H. \end{matrix}\right\}$

In 1865 Schorlemmer showed that there is no difference between the two groups, since under the action of chlorine both dimethyl and ethyl hydride give ethyl chloride, and ethylamyl gives heptyl chloride $C_7H_{15}Cl$.

The organo metallic compounds were discovered by Frankland in the course of his attempts to isolate the alcohol radicals. The following equations show the course of the reaction.

$$\underset{\text{Methyl iodide}}{CH_3I} + Zn. = \underset{\text{Zinc methiodide}}{Zn.(CH_3I)}$$

$$2\,Zn.(CH_3)I = \underset{\text{Zinc methyl}}{Zn.(CH_3)_2} + Zn.I_2$$

These compounds are very important as they are frequently used to prepare other substances.

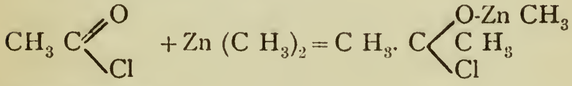
They give hydrocarbons when decomposed by water.

$$Zn.(C_2H_5)_2 + 2\ H_2O = Zn\ (OH)_2 + 2C_2H_6$$

or when acted upon by the alkyl halogen compounds

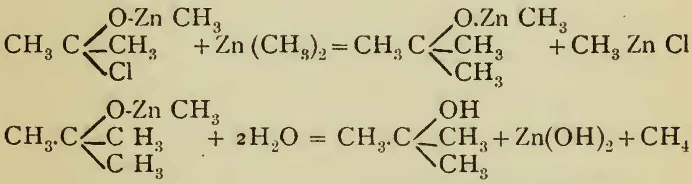
$$2\ CH_3I + Zn\ (CH_3)_2 = 2\ C_2H_6 + Zn\ I_2$$

They react with the chloride of a fatty acid giving (1) a secondary or tertiary alcohol when excess of the zinc alkyl compound is used.



$$CH_3\ C\left\langle\begin{matrix} O \\ Cl \end{matrix}\right. + Zn\ (CH_3)_2 = CH_3.\ C\left\langle\begin{matrix} O\text{-}Zn\ CH_3 \\ CH_3 \\ Cl \end{matrix}\right.$$

acetyl chloride

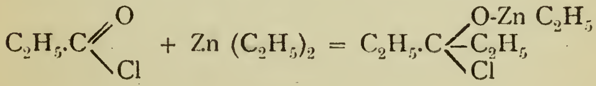


$$CH_3\ C\left\langle\begin{matrix} O\text{-}Zn\ CH_3 \\ CH_3 \\ Cl \end{matrix}\right. + Zn\ (CH_3)_2 = CH_3\ C\left\langle\begin{matrix} O.Zn\ CH_3 \\ CH_3 \\ CH_3 \end{matrix}\right. + CH_3\ Zn\ Cl$$

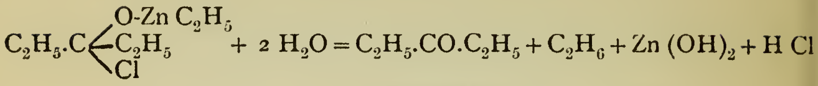
$$CH_3.C\left\langle\begin{matrix} O\text{-}Zn\ CH_3 \\ CH_3 \\ CH_3 \end{matrix}\right. + 2H_2O = CH_3.C\left\langle\begin{matrix} OH \\ CH_3 \\ CH_3 \end{matrix}\right. + Zn(OH)_2 + CH_4$$

Trimethylcarbinol

(2) a ketone when the proportion of the zinc alkyl compound to the acid coloride is smaller



$$C_2H_5.C\left\langle\begin{matrix} O \\ Cl \end{matrix}\right. + Zn\ (C_2H_5)_2 = C_2H_5.C\left\langle\begin{matrix} O\text{-}Zn\ C_2H_5 \\ C_2H_5 \\ Cl \end{matrix}\right.$$



$$C_2H_5.C\left\langle\begin{matrix}O\text{-}Zn\ C_2H_5\\ C_2H_5\\ Cl\end{matrix}\right. + 2\ H_2O = C_2H_5.CO.C_2H_5 + C_2H_6 + Zn\ (OH)_2 + H\ Cl$$

Diethylketone.

The discovery of the zinc alkyl compounds was followed by the preparation of similar substances by various chemists in which other metals took the place of zinc. Frankland himself prepared tin, mercury, and boron compounds.

It was during his study of the organo-metallic compounds that Frankland conceived the doctrine of valency, which he formulated in a paper read to the Royal Society in 1852. "When the formulae of inorganic chemical compounds are considered, even a superficial observer is struck with the general symmetry of their construction ; the compounds of nitrogen, phosphorus, antimony and arsenic especially exhibit the tendency of these elements to form compounds containing three or five equivs. of other elements, and it is in these proportions that their affinities are best satisfied ; thus in the ternal group we have NO_3, NH_3, NI, NS_3, PO_3, PH_3, PCl_3, SbO_3, SbH_3, $SbCl_3$, AsO_3, AsH_3, $AsCl_3$, etc., and in the five-atom group NO_5, NH_4O, NH_4I, PO_5, PH_4I, etc. Without offering any hypothesis regarding the cause of this symmetrical grouping of atoms, it is sufficiently evident, from the examples just given, that such a tendency or law prevails, and that no matter what the character of the uniting atoms may be, the combining power of the attracting element, if I may be allowed the term, is always satisfied by the same number of these atoms. It was probably a glimpse of the operation of this law, amongst the more complex organic groups, which led Laurent and Dumas to the enunciation of the theory of types; and had not those distinguished chemists extended their views beyond the point to which they were well supported by then existing facts—had they not assumed that the properties of an organic compound are dependent upon the position and not upon the nature of its single atoms, that theory would undoubtedly have contributed to the development of the science to a still greater extent than it has already done."

Very little notice was taken of Frankland's doctrine of valency, and it was only when Kekulé applied it to elucidate the constitution of benzene and other carbon compounds, that its importance was recognised.

Frankland and Kolbe (1847) showed that cyanides when hydrolysed give fatty acids.

Frankland and Duppa were the first to use ethylacetoacetate to synthesise homologues of acetic acid, a method afterwards perfected by Wislicenus.

Frankland and Duppa synthesised leucic acid by treating ethyl oxalate with zinc ethyl, and showed that phosphorus pentachloride converts etherial salts of acids of the lactic acid series into etherial salts of acids of the acrylic acid series. They pointed out that the group CO(OH) occurs in almost all organic acids, and that they owe their acidity to the presence of this group.

FRIEDRICH AUGUST KEKULE

1829-1896

FRIEDRICH AUGUST KEKULE was born at Darmstadt, on September 7th, 1829.

Unlike Liebig, Kekulé's exceptional ability was manifest in his school days. He showed a special aptitude for drawing and mathematics, and passed the leaving examination of the Gymnasium of his native town in 1847.

Kekulé's father wished August to be an architect, and he went to the University of Giessen to study for that profession. While there he attended Liebig's lectures on chemistry, and became so interested in this subject that he resolved to devote his life to its study. In 1851 he went to Paris for a year to attend Dumas' lectures. There he met Würtz and others who have made their mark in chemistry, and became so friendly with Gerhardt that he was allowed to read this chemist's famous "Traité de Chimie Organique" before it appeared in print.

In 1852 Kekulé graduated as Doctor of Philosophy at Giessen, and in 1854 he met Williamson. Speaking of his early years Kekulé said: "Originally a pupil of Liebig, I had become a pupil of Dumas, Gerhardt, and Williamson: I no longer belonged to any school."

In 1858 Kekulé was appointed Professor of Chemistry at the University of Ghent, and many young Germans, including Baeyer and Ladenburg, went there to study under their fellow-countryman.

In 1867 Kekulé left Ghent to take up the duties of Professor of Chemistry at the University of Bonn. He died July 13th, 1896.

The last twenty years of Kekulé's life were clouded by bad health; he also became deaf, and felt the infirmity most keenly. The early decay of Kekulé's physical powers was no doubt the result of excessive study. He confessed that for many years he only allowed himself three or four hours sleep in the twenty-four, and sometimes he would spend one, two and even three whole nights in succession over his books.

He became a member of the Royal Society

in 1875, and received the Copley Medal in 1885, and belonged to most of the learned societies of Europe.

Kekulé's most important work was in the realm of theoretical chemistry.

Dumas' Type Theory was an attempt to group together similar compounds. Gerhardt greatly extended and improved this theory by blending it with the radical theory, though he discarded the term *radical* and introduced that of *residue.* In the formation of ethyl nitrate from ethyl alcohol

$$C_2H_5{\cdot}OH + HNO_3 = C_2H_5{\cdot}NO_3 + H_2O$$

Gerhardt supposed nitric acid to give off an atom of hydrogen, leaving the residue NO_3, and ethyl alcohol to split up into the groups or residues OH and C_2H_5. The residue OH united with the atom of hydrogen to form water, and the two residues C_2H_5 and NO_3 united to form ethyl nitrate.

Although Gerhardt's "residues" were in many cases identical as regards atomic composition with the older radicals, the two conceptions were different, inasmuch as radicals were supposed to be capable of existing alone, while residues were not.

Hofmann pointed out that amines may be looked upon as ammonia in which one, two or three hydrogen atoms are replaced by a corresponding number of radicals, and Williamson (1850) showed that alcohol and ether can be regarded as water in which hydrogen atoms (one in the case of alcohol, and two in the case of ether) are replaced by alkyl radicals. Gerhardt referred organic compounds to four types: hydrogen, hydochloric acid, water, and ammonia. The following are examples of these types :

Hydrogen.	Hydrochloric Acid.	Water.	Ammonia.
$\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}$	$\left.\begin{matrix}\mathrm{H}\\\mathrm{Cl}\end{matrix}\right\}$	$\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}$	$\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{N}$
$\left.\begin{matrix}\mathrm{C\,H_3}\\\mathrm{C\,H}\end{matrix}\right\}$ Methane.	$\left.\begin{matrix}\mathrm{C\,H_3}\\\mathrm{Cl}\end{matrix}\right\}$ Methyl Chloride.	$\left.\begin{matrix}\mathrm{C_2H_5}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}$ Alcohol.	$\left.\begin{matrix}\mathrm{C_2H_5}\\\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{N}$ Ethylamine
$\left.\begin{matrix}\mathrm{C\,H_3}\\\mathrm{C\,H_3}\end{matrix}\right\}$ Ethylene.	$\left.\begin{matrix}\mathrm{C\;N}\\\mathrm{Cl}\end{matrix}\right\}$ Cyanogen Chloride	$\left.\begin{matrix}\mathrm{C_2H_5}\\\mathrm{C_2H_5}\end{matrix}\right\}\mathrm{O}$ Ether.	$\left.\begin{matrix}\mathrm{C_2H_3O}\\\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{N}$ Acetamide
$\left.\begin{matrix}\mathrm{C\,H_3O}\\\mathrm{C_2H_5}\end{matrix}\right\}$ Methyl Ethyl Ketone.		$\left.\begin{matrix}\mathrm{C_2H_3O}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}$ Acetic Acid.	

These formulae were not supposed to represent the arrangement of the atoms in the molecule, but to call to mind the formation and reactions of the various compounds symbolised.

Later on condensed types were introduced. Under the double water type $\left.\begin{matrix} H_2 \\ H_2 \end{matrix}\right\} O_2$ were placed

$$\left.\begin{matrix} S\,O_2 \\ H_2 \end{matrix}\right\} O_2 \text{ sulphuric acid}$$

$$\left.\begin{matrix} C_2\,O_2 \\ H_2 \end{matrix}\right\} O_2 \text{ oxalic acid}$$

and under the triple water type:

$$\left.\begin{matrix} H_3 \\ H_3 \end{matrix}\right\} O_3 \text{ was placed } \left.\begin{matrix} C_3\,H_5 \\ H_3 \end{matrix}\right\} O_3 \text{ glycerol}$$

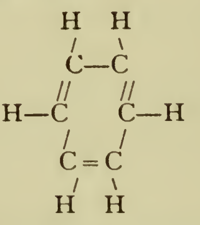
The following is an example of a mixed type.

$$\begin{matrix} \left.\begin{matrix} Cl \\ H \end{matrix}\right\} \text{hydrochloric acid} & & \left.\begin{matrix} Cl \\ S\,O_2 \end{matrix}\right\} \text{chlorsulphonic acid} \\ \left.\begin{matrix} H \\ H \end{matrix}\right\} O & \begin{matrix} + \\ \text{water type} \end{matrix} & \left.\begin{matrix} H \end{matrix}\right\} O \end{matrix}$$

The condensed and mixed types familiarised chemists with the idea of groups able to replace more than one atom of hydrogen, for example $(S\,O_2)''$ and (C_3H_5).'''

Kekulé added Marsh gas $C\,H_4$ to Gerhardt's types.

Frankland, in 1852, pointed out that nitrogen, phosphorus, arsenic and antimony can unite with three or five equivalents of other elements. Kekulé 1857-8 enunciated the theory of valency. He said, "My views . . . have grown out of those of my predecessors and are based on them. There is no such thing as absolute novelty in the matter." But although the writings of Williamson, Odling and others may contain the germs of the theory of valency, it needed a Kekulé to unearth them, and to present the theory in such a clear and convincing manner as to win at once a large body of adherents. The idea of the linking of the carbon atoms to form open and closed chains was entirely Kekulé's own, and we owe to him the first benzene formula (1865)



Many years afterwards he gave the following somewhat whimsical account of its origin. "I was sitting writing at my text-book; but the work did not progress, my thoughts were elsewhere. I turned my chair to the fire and dozed;

... the atoms were gambolling before my eyes ... long rows ... all turning and twisting in snake-like motion. But look! What was that? One of the snakes had seized hold of its own tail, and the form whirled mockingly before my eyes. As if by a flash of lightning I awoke, and ... spent the rest of the night in working out the consequences of the hypothesis."

In his paper "On the Constitution of the Aromatic Compounds" he foretells from his formula how many different substitution products of benzene are possible, discusses the homologues of benzene, and gives the law of their oxidation.

This paper had an immense influence on organic chemistry and has been designated by Professor Japp as "The most brilliant piece of scientific prediction to be found in the whole range of organic chemistry. What Kekulé wrote in 1865 has since been verified in every essential particular. ... Moreover, the theory has shown itself capable of boundless development. ... The debt which both chemical science and chemical industry owe to Kekulé's benzene theory is incalculable."

DMITRI IVANOWITSH MENDELEEFF

1834-1907

DMITRI IVANOWITSH MENDELEEFF was born the 7th February (N.S.) 1834, at Tobolsk in Siberia. His father was Director of the Gymnasium there, but soon after the birth of Dmitri he became blind, and had to resign his post. Fortunately his wife was a woman of exceptional energy and ability. When her husband was no longer able to work she opened and managed glass works at Tobolsk, and the enterprise succeeded so well that she was able to support and educate her large family of seventeen children.

Dmitri was educated at the Gymnasium in his native town till he was sixteen years old, when he entered the Institute at St. Petersburg to train for a Government teacher.

His first post was at Simferopol, in the

Crimea, but in 1856 he was admitted to the degree of Magister Chemiae of the University of St. Petersburg, and was made Privat-Docent in the University. In 1859 he obtained permission from the Minister of Public Instruction to travel, and fitted up a small laboratory at Heidelberg for his own use. He returned to Russia in 1861, and two years afterwards was appointed Professor of Chemistry at the Technological Institute of St. Petersburg. In 1866 he was appointed Professor of Chemistry at the University, and subsequently received the degree of Doctor of Chemistry. He died February 2nd (N.S.), 1907.

In 1882 he was awarded the Davy Medal by the Royal Society, and in 1889 the Faraday Medal by the Chemical Society of which he was an Honorary Fellow.

Mendeleeff did important work in many branches of chemistry, but undoubtedly his greatest achievement was the formulation of the Periodic Law. Lothar Meyer and Mendeleeff arrived at this law independently about the same time (1869), but Mendeleeff's statement of it is rather different, and in some ways superior to that of Meyer.

The Periodic Law is fully explained in Mendeleeff's classical text-book, "Principles of Chemistry," published in 1869.

Ever since Dalton propounded his atomic theory and made his historical atomic weight determinations, chemists have arisen from time to time who have endeavoured to trace some general relationship between the elements and their atomic weights.

The first attempt was made by Prout (1815). He assumed the existence of a primordial form of matter, and tried to prove that the atomic weights of all the other elements are whole multiples of that of hydrogen.

Dr. Thomas Thompson was much attracted by Prout's theory, and made many atomic weight determinations in the endeavour to establish it, but Berzelius showed that Thompson's numbers were incorrect, and Prout's hypothesis was abandoned until Dumas revived it. This chemist differed from Prout in thinking that a quarter of the atomic weight of hydrogen is the unit of which all other atomic weights are multiples.

Stas made a large number of extremely accurate atomic weight determinations with the view of supplying reliable data on which to base any general principle connecting the elements with their atomic weights, and concluded, as the result of his work, that Prout's hypothesis was untenable.

Other chemists besides Prout drew attention to atomic weight relationships.

Döbereiner (1817), showed that some of the elements can be grouped into triads in which the atomic weight of the middle member is half the sum of the first and last, *e.g.*, calcium (40), strontium (87·5), barium (137·0). This is only approximately true when our modern numbers are used, the calculated atomic weight of strontium working out at 88·5 instead of 87·5.

Lenssen (1857), tried to group all the elements into triads. Pettenkofer (1850) attempted to group similar elements into arithmetical series, and Newlands (1864) enunciated his Law of Octaves. He arranged all the known elements in a series according to their atomic weights, and pointed out that, as a rule, counting from any one element, every eighth preceding or succeeding member resembled it more than the other elements, or, stated in other words, similar members occur in octaves.

Newlands had hit upon the right idea, but his Law attracted very little attention, and it was left for Lothar Meyer and Mendeleeff to establish the principle that "The properties of the elements are periodic functions of their atomic weights."

Table of the Elements in Accordance with Mendeleeff's Classification

	I.	II.	III.	IV.	V.	VI.	VII.
1.	Li	Na	K	Rb	Cs	—	—
2.	Be	Mg	Ca	Sr	Ba	—	—
3.			Sc	Yt	La	Yb	—
4.			Ti	Zr	Ce	—	Th
5.			V	Nb	—	Ta	—
6.			Cr	Mo	—	W	U
7.			Mn	—	—	—	—
8.			Fe	Ru	—	Os	Transition elements.
			Co	Rh	—	Ir	
			Ni	Pd	—	Pt	
1.			Cu	Ag	—	Au	
2.			Zn	Cd	—	Hg	
3.	B	Al	Ga	In	—	Tl	
4.	C	Si	Ge	Sn	—	Pb	
5.	N	P	As	Sb	—	Bi	
6.	O	S	Se	Te	—	—	
7.	F	Cl	Br	I	—	—	

In the above table the elements are arranged in the order of their atomic weights, beginning at the top of the left hand column, proceeding down to the bottom, and then to the top of the next column, and so on.

When arranged in this way elements having similar chemical properties fall into the same horizontal row, and the members of horizontal rows in the top and bottom groups, which begin with the same number, are somewhat similar, though the resemblance is not so close as between members of the same row.

Elements in any two horizontal rows beginning with the same number have the same valency and form similar compounds.

1.	$LiCl$	$NaCl$	$RbCl$	$CsCl$		
1.		$CuCl$	$AgCl$	$AuCl$		
2.	$BeCl_2$	$MgCl_2$	$CaCl_2$	$SrCl_2$	$BaCl_2$	
2.			$ZnCl_2$	$CdCl_2$	—	$HgCl_2$

A vertical column is called a *period.* The first two periods are short ones and contain only seven elements each; the remaining periods are long ones, and when complete consist of seventeen members. There is no sudden change of properties, chemical or physical, in a single period, but a gradual variation.

In every period the valency of the first four members increases regularly from 1 to 4, from this point onwards the valency increases to 7 and also decreases to 1, the last three members having two valencies.

For example :

I	Na_2O	$Na\ Cl$	
II	Mg_2O_2	$Mg\ Cl_2$	
III	Al_2O_3	$Al\ Cl_3$	
IV	Si_2O_4	$Si\ Cl_4$	$Si\ H_4$
V & III	P_2O_5 & P_2O_3	PCl_5 & PCl_3	$P\ H_3$
VI & II	S_2O_6	—	$S\ H_2$
VII & I	Cl_2O_7 & Cl_2O	—	$Cl\ H$

The periodic character of the properties of the elements is shown very clearly by their atomic volumes. The atomic volume of an element is given by the quotient of the atomic weight by the specific gravity.

$$\text{Atomic volume} = \frac{\text{atomic weight}}{\text{specific gravity}}$$

Lothar Meyer was the first to draw attention to the relations between the atomic volumes of the elements. He drew a curve with atomic weights for abscissae and atomic volumes for ordinates, The curve consists of a series of undulations, and elements with similar chemical properties occur at similar parts of the curve. For instance, the members of the first horizontal line in the periodic table, Li, Na, K, Rb, Cs, occur at maximum points. The acid-forming elements, Cl, Br, I, lie on ascending parts of the curve to the left of K, Rb, Cs, respectively, while the basic alkaline earth metals Ca, Sr, Ba, lie on the descending parts to the right.

Most other physical properties are periodic, *e.g.*, melting point, magnetic power, etc. The atomic heat (product of specific heat and atomic weight) is approximately constant (6·4) and forms the only notable exception to the above rule.

In order to make the elements fall into suitable positions in the periodic table, Mendeleeff had to leave many blanks, which he believed would be filled up by elements unknown at that time. Owing to the regular character of the relations between neighbouring members, Mendeleeff was able to foretell many of the properties of the elements that would fill up the blanks. The discovery of gallium, scandium, and germanium with properties in close agreement with those predicted by Mendeleeff has strongly confirmed the exactitude and generality of the periodic law.

This law has proved very valuable for correcting atomic weights. For instance, Mendeleeff doubled the atomic weight of unranium (an alteration which has been justified by the researches of Zimmermann) and increased the atomic weight of indium from 75·6 to 114.

Mendeleeff did very important work on physical chemistry. He began his researches on specific volumes as early as 1855, and continued to work at this subject intermittently till 1870. He showed that in the case of homologous liquids the expansion coefficient diminishes in a regular manner as the series is ascended. He worked at the thermal expansion of liquids above their boiling points, and found that the formulae given by Kopp and others for calculating the expansion of liquids up to their boiling points hold good for higher temperatures.

In 1884 Mendeleeff developed the formula $\frac{1}{V} = 1 - kt$ where $V_0 = 1$ & V_t = required volume at t^0, and k is different for different substances but constant for any one substance between 0° and the neighbourhood of its boiling point. The results calculated from this formula agree fairly well with those found by experiment, and the equation would probably be strictly true for an ideal liquid.

He studied the specific gravities of aqueous solutions of alcohol, and came to the conclusion that three definite hydrates, $Et.HO.12H_2O$; $Et.HO.3H_2O$; $3EtHO.H_2O$, exist in aqueous solutions of ethyl alcohol. He published the result of his researches in 1889, and Professor Thorpe, writing in 1889, says, "This volume, the fruit of many years of labour, is unquestionably one of the most important contributions to the theory of solutions yet given to science."

In 1871 Mendeleeff began to work at the elasticity of gases at low pressures, *i.e.*, below one atmosphere.

Regnault had made researches on this subject and had shown no gas exactly obeys Boyle's Law, $pv=constant$, but that between 1 and 30 atmospheres the volume decreases too much except in the case of hydrogen, when it does not decrease enough. Mendeleeff predicted that at higher pressures all other gases would behave in the same way as hydrogen, and that the volume would not decrease with increased pressure as much as the law required. Amagat and Cailletet have found this to be the case.

Mendeleeff examined the variation of volume with pressure at low pressures, *i.e.*, below one atmosphere, and found that for very low pressures, as for very high ones, the volume did not diminish as much as required by the law. He determined the real coefficient of thermal expansion of many gases, and showed that the coefficient increases with increasing molecular weight, and that the coefficient is the same for gases with the same molecular weight.

Many Russian industries are indebted to Mendeleeff, especially the petroleum industry of Baku, which has attained its present prosperous condition mainly owing to the exertions of this famous chemist.

Professor Thorpe pays the following tribute to Mendeleeff:

"No man in Russia has exercised a greater or more lasting influence on the development of physical science than Mendeleeff. His mode of work and of thought is so absolutely his own, the manner of his teaching and lecturing is so entirely original, and the success of the great generalisation with which his name and fame are bound up is so strikingly complete, that to the outer world of Europe and America he is to Russia what Berzelius was to Sweden, or Liebig to Germany, or Dumas to France."

WILLIAM HENRY PERKIN

1838-1907

William Henry Perkin, the youngest son of a builder and contractor, was born in London, March 12th, 1838.

When he was nearly thirteen years old a young companion showed him some chemical experiments, which so impressed and delighted him that he determined forthwith to be a chemist.

About this time he left the private school he had been attending to enter the City of London School. Science was not included amongst the regular subjects of instruction, but Thomas Hall, one of the masters and a pupil of Hofmann's, gave two lectures a week on chemistry and philosophy in the interval between morning and afternoon school. Young Perkin was a most enthusiastic pupil, and was soon allowed to act as laboratory assistant.

The elder Perkin had cherished the hope that his son would become an architect, but when he found that the youth's desire to follow chemistry as a profession grew stronger and stronger, he withdrew his opposition and allowed Henry to enter the Royal College of Chemistry in 1853.

Perkin speedily acquired dexterity in the ordinary processes of qualitative and quantitative analysis, and Hofmann, recognising his exceptional ability, promoted him to research work before the end of his second year. His first task was to prepare a nitro derivative of anthracene, but he was unable to accomplish it. He was then set to study the action of cyanogen chloride on napthylamine, and he conducted this research so successfully that Hofmann appointed him a member of his regular research staff, and gave him work to do in conjunction with A. H. Church.

In 1856 Perkin discovered mauve, and so laid the foundation of the coal-tar colour industry, which has become so important. He began building a factory at Greenford Green, near Sudbury, for the preparation of mauve, in June 1857, and some six months later the new dyestuff was put on the market. His business venture proved so successful that he was able to retire in 1874. He continued to live at Sudbury, and conducted his researches in a private laboratory adjacent to his house. He married twice, and his three sons have all attained success as chemists.

Perkin became a Fellow of the Royal Society in 1866, was awarded the Davy Medal in 1889, and was the recipient of many honorary degrees and medals both English and foreign. He was made a knight in 1906, and in July of that year a great international meeting was held in London to celebrate the fiftieth anniversary of the discovery of mauve. In the autumn Perkin went to America to be present at the Jubilee celebrations held there in his honour. He died July 14th, 1907.

It has already been mentioned that in 1855 Perkin was made a member of Hofmann's research staff, but the work he did for Hofmann by no means exhausted the young man's energy, and he fitted up a room at home in which he carried out researches of his own in the evenings and during the College holidays. It was in this primitive home laboratory that he discovered mauve in the Spring of 1856.

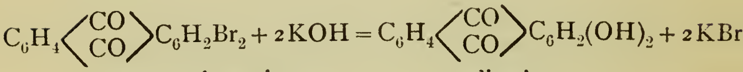
He attempted to synthesise quinine by oxidising a salt of allyltoduidine with potassium dichromate, but instead of quinine he obtained a "dirty reddish brown precipitate." He was sufficiently interested in this coloured precipitate to try the effect of the same oxidising agent on the salt of a simpler base, aniline. This time he obtained a very dark coloured precipitate, which he found had the properties of a dye. He induced Messrs Pullar of Perth to experiment with it (mauve), and they expressed the opinion that if not too expensive the new dye might be valuable. Encouraged by Messrs Pullar's report, Perkin took out a patent for mauve, and resolved to attempt to prepare it on a manufacturing scale. His father gave nearly all his life's savings to build a factory at Greenford Green near Sudbury, and his brother Thomas joined in the enterprise. The new dye was brought out under the name of "Aniline Purple" or "Tyrian Purple."

Perkin had innumerable obstacles to overcome, which he describes in the following words :

" In the case of this new colouring matter, not only had the difficulties incident to its manufacture to be grappled with, and the prejudices of the consumer overcome, but owing to the fact that it belonged to a new class of dyestuffs a large amount of time had to be devoted to the study of its applications to dyeing, calico printing, etc. It was, in fact, all pioneering work—clearing the road, as it were, for the introduction of all colouring matters which followed, all the processes worked out for dyeing silk, cotton, and wool, and also for calico printing, afterwards proving suitable for magenta, Hofmann violet, etc." (Hofmann Memorial Lecture).

After a time mauve was superseded by other violet dyes, but Perkin moved with the times, and devised processes for producing the new dyes in his factory.

In 1868 Graebe and Liebermann synthesised alizarin (a valuable dye which occurs in madder root) by fusing *α β* dibromanthraquinone with potash.

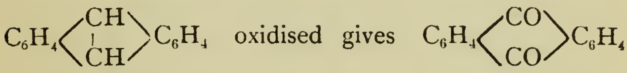


$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_2Br_2 + 2KOH = C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_2(OH)_2 + 2KBr$$

dibromanthraquinone alizarin.

Although Graebe and Liebermann's method was patented in Germany and Great Britain, the cost of producing the artificial alizarin was too great to make the method a commercial success, so Perkin began researches with the object of finding a cheaper way of preparing this dye, and succeeded so well that in 1869 he was able to take out patents for two new methods, the anthraquinone process, and the dichloroanthracene process. The first method, which is the one used at the present day, was patented almost at the same time by Graebe and Liebermann, who had worked it out independently.

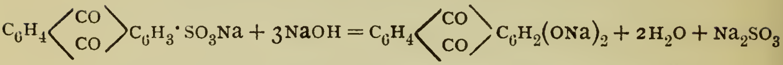
In this method anthracene is first oxidised to anthraquinone with sodium dichromate and sulphuric acid.



$$C_6H_4\left\langle\begin{matrix}CH\\ |\\ CH\end{matrix}\right\rangle C_6H_4 \quad \text{oxidised gives} \quad C_6H_4\left\langle\begin{matrix}CO\\ CO\end{matrix}\right\rangle C_6H_4$$

anthracene anthraquinone

The anthraquinone is next sulphonated by heating with fuming sulphuric acid; the mixture is then diluted, filtered, and treated with soda, when sodium anthraquinone monosulphonate crystallises out, being less soluble than the sodium salts of the disulphonic acids, which are also present in the solution. The sodium anthraquinone monosulphonate is fused with soda, and a small quantity of potassium chlorate, to convert it into the sodium salt of alizarin.



$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_3\cdot SO_3Na + 3NaOH = C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_2(ONa)_2 + 2H_2O + Na_2SO_3$$

Alizarin $C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_2(OH_2)$ is precipitated from the sodium salt by hydrochloric acid.

When Perkin commenced to manufacture alizarin by the anthraquinone process he used ordinary strong sulphuric acid, which gave a mixture of alizarin, anthrapurpurin and flavopurpurin for the final product. He found that a better yield and purer product could be obtained by using Nordhausen sulphuric acid, but as this acid was then very difficult to obtain he tried another process, the dichloroanthracene process. Dichloroanthracene is more readily sulphonated than anthraquinone, and ordinary strong sulphuric acid is sufficient to bring about sulphonation. The chief product is a disulphonic acid which, by a similar treatment to that carried out in the anthraquinone process, yields eventually anthrapurpurin, together with a small quantity of flavopurpurin.

The rapid increase in the demand for artificial alizarin is told by Perkin in the following words:

"Before the end of the year (1869) we had produced one ton of this colouring matter in the form of paste; in 1870, forty tons, and in 1871 two hundred and twenty tons, and so on in increasing quantities year by year." (Hofmann Memorial Lecture).

By 1873 the demand had outgrown the producing power of the Greenford Green Factory, and the business was sold to Messrs Brooke, Simpson and Spiller, and Perkin retired, having made sufficient to live upon.

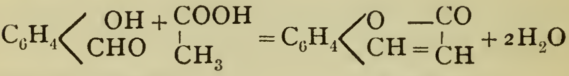
Throughout his business career Perkin devoted as much time to research as possible, and in 1858, in conjunction with Duppa, he prepared amido-acetic acid, or glycocoll $C\ H(NH_2)COOH$ by heating bromoacetic acid with ammonia. This was the first time this substance had been prepared synthetically. A little later he and Duppa worked at the relationship between tartaric acid, and fumaric and maleic acids, and synthesised tartaric acid by heating dibromosuccinic acid with moist silver oxide.

$$\begin{array}{l} CH.Br.COOH \\ | \\ CH.Br.COOH \end{array} + 2AgOH = \begin{array}{l} CH(OH)COOH \\ | \\ CH(OH)COOH \end{array}$$

dibromosuccinic acid

tartaric acid.

Perkin synthesised coumarin, the substance to which sweet woodruff owes its pleasant odour, by heating salicylic aldehyde with sodium acetate and acetic anhydride.



$$C_6H_4\left\langle\begin{matrix}OH\\CHO\end{matrix}\right. + \begin{matrix}COOH\\|\\CH_3\end{matrix} = C_6H_4\left\langle\begin{matrix}O & -CO\\ & |\\CH & = CH\end{matrix}\right. + 2H_2O$$

salicylic aldehyde Coumarin.

He prepared cinnamic acid by heating benzaldehyde with sodium acetate and acetic anhydride. The sodium salt of β phenylhydracrylic acid is formed as an intermediate product, which is then deprived of water by the acetic anhydride. Writing the acids instead of the sodium salts for the sake of simplicity the equations are,

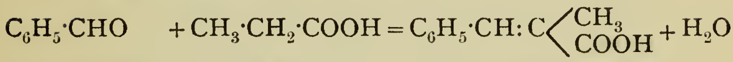
$$C_6H_5{\cdot}CHO + CH_3{\cdot}COOH = C_6H_5{\cdot}CH(OH)CH_2{\cdot}COOH$$

β phenylhydracrylic acid

$$C_6H_5{\cdot}CH(OH)CH_2{\cdot}COOH = C_6H_5\,CH:CH{\cdot}COOH + H_2O$$

cinnamic acid.

This method, which is known by the name of "Perkin's synthesis," is a very valuable one, since all aromatic aldehydes (and hydroxyaldehydes) act in a similar way with the sodium salt of acetic acid or of one of its homologues. In the case of the higher fatty acids, condensation always takes place between the oxygen atom of the aldehyde group and the two hydrogen atoms of the CH_2 group, which are united to the carboxyl group



$$C_6H_5{\cdot}CHO + CH_3{\cdot}CH_2{\cdot}COOH = C_6H_5{\cdot}CH{:}C\langle\begin{matrix}CH_3\\COOH\end{matrix} + H_2O$$

benzyaldehyde propionic acid phenylmethylacrylic acid

$$C_6H_4(OH){\cdot}CHO + CH_3{\cdot}COOH = C_6H_4(OH)CH : CH{\cdot}COOH$$

salicylaldehyde coumarinic acid

In 1881 Perkin began to make experiments on the magnetic rotatory power of substances, a subject to which he devoted attention during the rest of his life. Michael Faraday in 1846 showed that some optically inactive substances acquire the power of rotating the plane of polarisation when brought into a magnetic field, and Perkin showed that the extent of the rotation depends upon the constitution of the compound. He found that the molecular magnetic rotatory power is an additive property in homologous series, and that an increase of 1·023 units is produced by the addition of every CH_2 group.

The molecular rotation of any substance can be expressed by

$$a + n\,(1{\cdot}023)$$

where *a* is constant for any given homologous series, but differs in value according to the series considered, and n is the number of CH_2 groups in the molecule. The constant a depends upon constitution and is different for normal and iso compounds. Professor J. W. Brühl of Heidelberg paid the following tribute to the value of Perkin's work on this subject, in a letter addressed to him on the occasion of the Jubilee celebrations of 1906. "Availing yourself of the marvellous discovery of your great countryman, Michael Faraday, you undertook to investigate the relations between the chemical composition of bodies and their magnetic circular polarisation—that is to say, one of the general properties of all matter. Before you began work there was little, almost nothing, known of this subject, certainly nothing of practical use to the chemist. You created a new branch of science, taught us how, from the magnetic rotation, conclusions can be drawn as to the chemical structure of bodies, and showed that the magnetic rotation allows us to draw comprehensive and certain conclusions as to the chemical constitution of substances, just as we may from another general physical property, viz., refraction and dispersion. And by showing that both these physical methods of investigation lead to completely harmonious results, you did essential service to both the branches of study, and also to chemistry, which they are destined to serve."

John Hall Gladstone was the chemist with whom Perkin compared his results. They published a joint paper in 1889, "On the Correspondence between the Magnetic Rotation and the Refraction and Dispersion of Light by Compounds containing Nitrogen."

VICTOR MEYER

1848-1897

VICTOR MEYER was the son of a calico manufacturer, and was born in Berlin, 18th September, 1848. His mother was a very intellectual woman, and inspired her son with literary and artistic tastes. As a young man Victor wished to be an actor, and no doubt he would have achieved success in that profession if he had followed it, for he was handsome, and had a good voice and an artistic temperament.

In 1864 he attended some of Hofmann's lectures in Berlin, and in 1865 he entered Heidelberg University, and had the good fortune to study under Bunsen, Kopp, Kirchhoff and Helmholtz, all brilliantly clever men.

Although Meyer was one of the youngest students in the University, Bunsen made him one of his assistants, and employed him to analyse some mineral waters. This work was excellent training, but it was not very congenial to a young man thirsting to do original work, so Meyer resigned his post in 1868, and entered Baeyer's little laboratory in Berlin. He remained with Baeyer for three years, and then took a post under Fehling at Stuttgart. He had only been there a year when he was invited to become Director of the chemical laboratory at Zürich Polytechnic. He could scarcely have hoped for better fortune. Only twenty-four, and yet placed at the head of a convenient laboratory attended by plenty of students, able and anxious to carry out the researches indicated by their Professor. Meyer made good use of his opportunities, and at the end of the thirteen years spent at Zürich, he was known as one of the foremost investigators of the day.

In 1885 he went to Göttingen. In 1889, when Bunsen retired from his position at the Heidelberg University, he expressed the wish that his old pupil, Victor Meyer, should succeed him. So Meyer left Göttingen to take up his new duties at Heidelberg. He remained there until his death, August 8th, 1897.

One of Meyer's most important researches was that on the nitro-paraffins. His first memoir on this subject was published in 1874, and was entitled "On the nitro-compounds of the Fatty Series." Meyer, in conjunction with his pupils, made a most exhaustive research on these compounds, extending over a period of about twenty years.

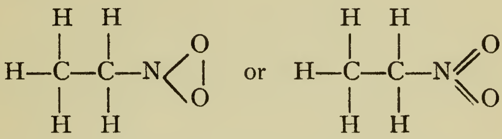
Mitscherlich had prepared nitro-benzene in 1834, and Meyer thought that the paraffins ought to yield a series of similar compounds. He experimented with amyl iodide and silver nitrite, and obtained a colourless liquid, boiling between 150° and 160°, which proved on analysis to have the formula $C_5H_{11}NO_2$ and was therefore isomeric with amyl nitrite boiling at 99°. He found that a whole series of alkyl nitro compounds existed isomeric with the corresponding etherial salts of nitrous acid, and that they could be prepared by acting on the various alkyl iodides with silver nitrite.

$$RI + AgNO_2 = R.NO_2 + AgI$$

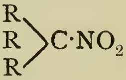
where R = alkyl radical.

The nitro compounds are not readily hydrolysed, and when reduced they give the corresponding amines. $CH_3{\cdot}NO_2$ gives CH_3NH_2

therefore nitrogen is probably linked to carbon. For example, the constitutional formula of nitro ethane is

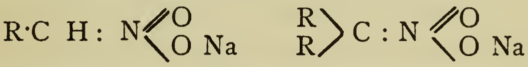


Nitro compounds may be divided into

Primary	Secondary	Tertiary
$R{\cdot}CH_2NO_2$	 $\left.\begin{matrix}R\\R\end{matrix}\right\rangle CH{\cdot}NO_2$	 $\left.\begin{matrix}R\\R\\R\end{matrix}\right\rangle C{\cdot}NO_2$

The primary and secondary compounds possess slight acidic properties and react with alcoholic sodium hydroxide, giving metallic derivatives R. C H Na N O_2 and $\left.\begin{matrix}R\\R\end{matrix}\right\rangle C\ Na\ N\ O_2$

Later research has shown that it is highly probable that the constitution of these salts is



$R{\cdot}C\ H:N\left\langle\begin{matrix}O\\O\ Na\end{matrix}\right. \qquad \left.\begin{matrix}R\\R\end{matrix}\right\rangle C:N\left\langle\begin{matrix}O\\O\ Na\end{matrix}\right.$

and that they are derived from an iso-nitro compound isomeric with the true nitro-paraffins.

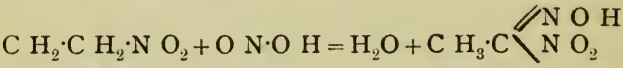
Meyer and his pupils found that the primary compounds will react with bromine, giving a monobrome derivative which possesses acidic properties, and a dibrome derivative which is neutral

$$R{\cdot}CHBrNO_2 \qquad\qquad R{\cdot}CBr_2NO_2$$

The monobrome compound gives a metallic derivative $R{\cdot}CNaBrNO_2$ Secondary nitro-compounds give a monobrome derivative which is neutral $\begin{matrix}R\\R\end{matrix}\!\!>C{\cdot}Br{\cdot}NO_2$ and tertiary compounds do not react with bromine at all.

The nitro compounds react in a very interesting manner with nitrous acid.

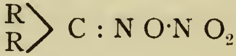
The *primary* nitro compounds when dissolved in potash, mixed with an alkaline nitrite and treated cautiously with sulphuric acid, added drop by drop, give a blood-red colouration which disappears on the further addition of acid. If the solution is then shaken with ether a nitrolic acid is obtained



$$CH_2{\cdot}CH_2{\cdot}NO_2 + ON{\cdot}OH = H_2O + CH_3{\cdot}C\begin{matrix}/\!\!/NOH\\ \diagdown NO_2\end{matrix}$$

nitro-ethane ethyl-nitrolic acid

The nitrolic acids are sweet in taste, readily soluble in water, strongly acid, and usually easily crystallisable. They dissolve in alkalies giving a red solution.

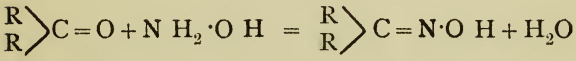
The *secondary* compounds when treated with nitrous acid give a deep blue colouration, and insoluble compounds are formed called pseudonitroles isomeric with the nitrolic acids. They may have the constitution  $\begin{array}{l}R\\R\end{array}\rangle C:NO\cdot NO_2$

The *tertiary* compounds do not react with nitrous acid.

Meyer, in conjunction with Janny, studied the action of hydroxylamine on aldehydes and ketones, and discovered the two series of compounds known as the aldoximes and ketoximes

$$R\cdot C\left\langle\begin{array}{l}H\\O\end{array}\right. + NH_2\cdot OH = R\cdot C\left\langle\begin{array}{l}H\\N.OH\end{array}\right. + H_2O$$

an aldehyde hydroxylamine an aldoxime

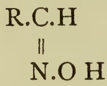


$$\begin{array}{l}R\\R\end{array}\rangle C=O+NH_2\cdot OH = \begin{array}{l}R\\R\end{array}\rangle C=N\cdot OH+H_2O$$

A ketone A ketoxime

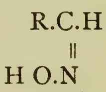
The oximes are substances of considerable importance.

They give many interesting derivatives, and as the above reaction shows the presence of a carbonyl group, it is sometimes made use of to decide questions of constitution. The stereochemistry of nitrogen may be said to have sprung from the discovery of the oximes, as aldoximes and ketoximes often exist in isomeric forms which can be most readily explained by assuming that the valencies of the nitrogen atom do not all lie in the same plane. Victor Meyer and Goldschmidt put forward this view. According to Hantzsch and Werner the two valencies uniting nitrogen to carbon lie in one plane, and the third valency of nitrogen in another



$$\begin{array}{l} \text{R.C.H} \\ \;\;\| \\ \;\;\text{N.O H} \end{array}$$

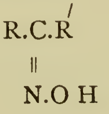
(1)



$$\begin{array}{r} \text{R.C.H} \\ \| \;\; \\ \text{H O.N} \;\; \end{array}$$

(2)

In the above figure the double bond may be supposed to lie in a plane at right angles to the plane of the paper, and the O H group to lie in proximity to the hydrogen atom in one isomeride (fig. 1) and to the alkyl group (fig. 2) in the other. A similar explanation applies to isomeric ketones.



$$\begin{array}{l} \text{R.C.}\overset{/}{\text{R}} \\ \;\;\| \\ \;\;\text{N.O H} \end{array}$$

(1)

$$\begin{array}{r} \text{R.C.}\overset{\backslash}{\text{R}} \\ \| \;\; \\ \text{H O.N} \;\; \end{array}$$

(2)

According to this theory when the two alkyl groups in a ketone, represented by R and $\overset{/}{R}$, are the same, the corresponding ketoxime should exist only in one form, and up to the present no isomeric forms have been met with. V. Meyer and Auwers differ from Hantzsch and Werner in believing that only the hydrogen atom, and not the whole hydroxyl group, lies outside the plane occupied by the other atoms in the molecule.

In 1877 Meyer perfected the method for measuring vapour density which is known by his name.

The apparatus consists essentially of two long tubes which fit one inside the other. A known weight of the substance whose vapour density is required is volatilised in the inner tube by means of the heat generated by a liquid boiling in the outer tube. The inner tube is furnished with a short delivering tube, which passes under a graduated tube filled with and inverted over water. The vapour of the given substance forces air out of the inner tube which passes down the delivery tube and displaces water in the graduated tube. The volume occupied by the air is observed, reduced to normal temperature and pressure, and a correction applied for the tension of aqueous vapour. This volume (v) is the same volume as that which the vapour of the given substance would occupy at N.T.P. Since the weight of 1c.c of hydrogen at N.T.P. is ·00009 grm. the weight of (v) volumes of hydrogen can be readily calculated, and the required vapour density is given by

$$\frac{\text{known wt. of substance taken}}{\text{wt. of (v) volumes of H.}}$$

The tubes are generally made of glass, but for very high temperatures glazed poreclain is used.

V. Meyer, in conjunction with Carl Meyer (no relation) made a great many density determinations with the apparatus described above. They found that arsenic and phosphorous at a white heat have densities corresponding with diatomic molecules, while zinc at 1400°C and bismuth at 1700°C have densities corresponding with monatomic molecules. In 1879 they showed that the halogens undergo dissociation at high temperatures. At 600°C the vapour density of iodine is 8·7 (air = 1) corresponding to diatomic molecules I_2, at 842°C it is 6·7 and at 1570°C 5·7, showing that a large portion of the molecules at this temperature become monatomic. V. Meyer and C. Langer found that bromine has a density of 5·52 up to about 900$_{\circ}$C when diluted with eleven times its volume of nitrogen, At 1200°C when diluted with five volumes of nitrogen the density of bromine fell to 4·3, and at a white heat to 3·6. The vapour density of chlorine remained constant at 2·45 up to 1200°C, and only fell to 2·02 at 1400°C.

In 1882, while giving a course of lectures on benzene derivatives, chance led Meyer to perhaps the most important of his many valuable discoveries.

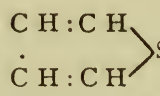
He wished to show his class Baeyer's indophenin reaction, supposed at that time to indicate the presence of benzene, and for this purpose he shook a little benzene with a small quantity of concentrated sulphuric acid and a trace of isatin, but to his surprise the expected blue colouration did not appear. Meyer's lecture experiments were almost invariably successful owing to the great pains he bestowed upon their preparation, so he was much surprised that this one proved a failure. Sandmeyer, who was at that time acting as Meyer's assistant, pointed out that ordinary coal-tar benzene had been used for the rehearsal experiment, while benzene prepared by heating benzoic acid with lime had been used for the lecture. Meyer at once followed up the suggested clue, and tested benzene prepared by every known method as well as many samples of coal-tar benzene, and he soon established the fact that only benzene derived from the latter source gave the indophenin reaction, and that it was due to a sulphur compound of some description present in coal-tar benzene. He found, moreover, that this sulphur compound was removed by repeated shaking with sulphuric acid.

He then shook 10 litres of benzene with sulphuric acid, distilled the product, and obtained a few cubic centimetres of a thin liquid containing sulphur, which boiled at about 83°C and which he afterwards called *thiophene.*

His next experiment was conducted on a much larger scale.

He shook 250 litres of coal-tar benzene with sulphuric acid, separated the acid layer which contained thiophene sulphonic acid together with a little benzene sulphonic acid, diluted with water, converted into the lead salt, and liberated the thiophene by distilling with ammonium chloride.

Thiophene



$$\left.\begin{array}{l} CH:CH \\ \cdot \\ CH:CH \end{array}\right\rangle S$$

is a thin, clear, mobile liquid with an odour resembling that of benzene.

It boils at 84°C and gives derivatives analogous to those of the benzene series. The chemistry of thiophene and its homologues is almost as extensive as that of benzene itself, so that Meyer's discovery resulted in the addition of a new section to organic chemistry.

The above is by no means an exhaustive account of Meyer's achievements.

He invented several useful pieces of apparatus, wrote papers on stereochemical questions, studied the conditions determining the gradual and explosive combustion of gaseous mixtures, determined the fusing points of many salts melting at high temperatures, discovered the iodonium compounds, and investigated many other substances too numerous to mention; indeed, he and his pupils contributed upwards of 300 memoirs and papers to chemical literature.

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